STELLINGEN

1. Bij de afleiding van de reactieconstanten van de oxydatie van zetmeel met HOCl/OCl$^-$ of HOBr/OBr$^-$ houden ondergenoemde auteurs ten onrechte geen rekening met het pH afhankelijke gedrag van het reagens, noch met het optreden van neven- en volgreacties.
   K.F. Patel et al., J. Appl. Polym. Sci. **18**, 389 (1989)
   J. Schmorak et al., Starch **14**, 278 (1962).
   I. Ziderman et al., Carbohydr. Res. **27**, 341 (1973).

2. Het calciumbindend vermogen van 2,3-dicarboxy-zetmeel wordt vooral bepaald door de oxydatiegraad en minder door de ketenlengte van het materiaal.
   M.S. Nieuwenhuizen, dissertatie Delft 1985, p.92.
   M. Floor, dissertatie Delft 1989, p. 111.

3. De mate waarin vertegenwoordigers van polycyclische aromatische koolwaterstoffen geadsorbeerd op aërosol worden omgezet door N_2O_5 hangt minder af van de chemische reactiviteit dan van de wateroplosbaarheid.
   J.N. Pitts, Jr. et al., Environ. Sci. Technol. **19**, 1115 (1985).

4. De relatief hoge concentratie chloroform in de atmosfeer, die door *Khalil* et al. wordt toegeschreven aan een flux uit de oceaan is mogelijk het gevolg van de omzetting van het in grote hoeveelheid geëmitteerde 1,1,1-trichloorethaan.
   M.A.K. Khalil et al., Tellus **35 B**, 266 (1983).

5. Bij het toetsen van de biodegradeerbaarheid van sterk metaalion complexerende stoffen moet bij de samenstelling van de testmedia volgens bijvoorbeeld de OECD-voorschriften, rekening worden gehouden met suppletie van calcium- en magnesiumionen.

6. Het mag opmerkelijk worden genoemd dat het inmiddels ruim 40 jaar oude leerboek "Organic Chemistry" van *Fieser* and *Fieser* probleemloos en vaak met profijt kan worden gebruikt.
   L.F. Fieser and *M. Fieser*, Organic Chemistry, second edition, Reinhold Publishing Company, New York (1950).

7. Bij een belangrijk deel van de gemelde effecten van microwave experimenten ontbreekt een nauwkeurige opgave van temperatuur en druk.

8. Het zou de veiligheid op laboratoria ten goede komen als de resultaten van op voorhand onverdachte, maar niettemin gevaarlijke experimenten in een daartoe geschikt tijdschrift worden gepubliceerd.

9. Het zou de bij een aanrijding betrokkenen verplicht moeten worden gesteld glasscherven op de weg op te ruimen ter voorkoming van hieruit voortvloeiend ongemak zoals lekke banden en van ongevallen ten gevolge van het "Lorelei-effect".

10. Onderwijs in vreemde talen zou kunnen worden vergemakkelijkt als bij het vak Nederlands meer aandacht wordt besteed aan etymologie.

11. De alant (*Inula helenium*) was zijn tijd vooruit.

12. Het is betreurenswaardig dat de negende symfonie van Beethoven niet meer heeft opgeleverd dan de norm voor de lengte van een compact plaat en niet de vervulling van het zo gewenste "alle Menschen werden Brüder".

A.C. Besemer.
Zeist, januari 1993.

THE BROMIDE-CATALYZED HYPOCHLORITE OXIDATION OF STARCH AND INULIN
Calcium complexation of oxidized fructans

PROEFSCHRIFT

ter verkrijging van de graad van doctor
aan de Technische Universiteit Delft
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in het openbaar te verdedigen ten overstaan van
een commissie aangewezen door het College van Dekanen
op maandag 18 januari 1993 te 16.00 uur

door

A.C. Besemer

geboren te Schiedam

Dit proefschrift is goedgekeurd door de promotor Prof. Dr. Ir. H. van Bekkum

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Ter nagedachtenis
aan mijn ouders.
Aan Elly, Jojanneke
Martijn, Marcel

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The drawing on the front cover represents the proposed conformation of a calcium dicarboxy-inulin complex. On the back cover an important source of inulin, chicory plants, are shown.

Drawing on the front cover: Jan Besemer.

CHAPTER 1

OXIDIZED CARBOHYDRATES AS BUILDERS IN DETERGENT FORMULATIONS

Introduction

It has been predicted [1-3] and indeed observed that the discharge of large amounts of phosphate-containing substances onto surface waters has led to an important environmental problem. Phosphate is a nutrient for algae and stimulates the growth of these organisms. Especially in waters in which high concentrations occur eutrophication will be the result or has in fact been observed. This gave rise to concern especially with respect to the Great Lakes of the US [4], South Africa [5], United Kingdom [6, 7], Germany [8] and Portugal [9]. Even in coastal areas and in seas eutrophication has been observed for instance in Japan [10], the North Sea [11] and the Adriatic Sea [12, 13]. An important though not major contribution to the phosphate load originates (or has been originating) from laundry detergent formulations, which contain(ed) substantial amounts of sodium tripolyphosphate (STP) as a so-called builder. Because of the presence of calcium and magnesium ions in water deposits of salts of these metals - called incrustation - on the fabrics may be formed during the washing process. By addition of sufficient sequestering agents the concentration of these ions will be lowered to an extent that incrustation is prevented. As mentioned STP [14] was used, and is still in use for this purpose because it combines a good performance and a low price.

It formed an important constituent (up to 50% by weight) of the detergent compositions. Worldwide production of laundry detergents has been estimated to be 30 million tons per year [14]. In 1982 according to estimates the consumption of STP in Europe amounted to 1,100,000 tons and in the United States 586,000 tons [14]. Worldwide use of STP was estimated [15] in 1982 8.2. 10^6 tons, in 1987 2.7. 10^6 and in 1990 2.5. 10^6 tons; the consumption in 1995 is expected to be 2.0. 10^6 tons.
Despite the possibility of eutrophication it took a long time before new builder systems as substitute for STP were introduced. The most important reason for the slow process of replacement is the fact that beside a good calcium and magnesium binding a substitute should meet the following requirements:

- biodegradable
- cheap
- non-toxic
- preferably water soluble.

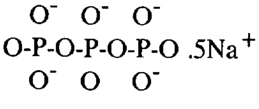
Many attempts have been undertaken for the development of an alternative for STP. Many of the organic compounds which have been synthesized exhibit good sequestering strength and capacity. Generally, molecules containing carboxylic acid and ether or acetal groups are concerned [16-18]. Only a few compounds fulfilled all requirements. In the next paragraphs we will discuss the properties of the calcium and magnesium sequestering agents, which are nowadays used in detergent formulations. In the framework of this thesis some new potentially attractive builder systems, based on carbohydrate derived compounds and materials will be discussed.

Survey of the commonly used builders and their properties

a. *(Penta)sodium tripolyphosphate (STP)*

STP (see Fig. 1) has various attractive properties:

- it is a good calcium sequestering agent ($\log K_{Ca} = 6.0$)
- it prevents the redeposition of suspended dirt particles
- it is cheap, toxicologically safe and good water soluble.



$$\begin{array}{l} \quad O^- \;\; O^- \;\; O^- \\ O\text{-}P\text{-}O\text{-}P\text{-}O\text{-}P\text{-}O\ .5Na^+ \\ \quad O^- \;\; O \;\;\; O^- \end{array}$$

Fig. 1. Sodium tripolyphosphate (STP).

In surface water STP will be slowly hydrolyzed; the estimated half-life is 1-3 years [19]. However, the rate is enhanced considerably by certain microorganisms [20]. The product, orthophosphate, is persistent and as mentioned above, being a nutrient for algae, it causes growth of these organisms, leading to eutrophication of stagnant waters, lakes and even seas [4-13]. Because of this drawback the use of STP has been forbidden or restricted by legislation or voluntary agreement in many countries [21].

b. Aminocarboxylic acids

In the group of aminocarboxylic acids several important representatives are found, the most important being nitrilotriacetic acid (NTA, see Fig. 2).

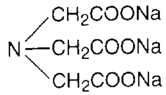


Fig. 2. Nitrilotriacetic acid (as trisodium salt).

Once NTA seemed to be the most promising phosphate substitute. The compound binds calcium and magnesium to a large extent. The complex constant of NTA is even somewhat higher than that of phosphate: log K_{Ca} = 6.6 [16, 18]. In numerous studies it has been shown that NTA is readily biodegradable.
Reviews on this subject are given by *Perry* et al. [22, 23]. However, there remain some reservations, which led to doubts about the safety of a large-scale use of NTA [22, 23]. For instance it was reported that exposure of rats and mice to NTA led to urinary tract cancer [24], that this compound has a chromosome-breaking effect [25] and exerts cytogenic [26], co-carcinogenic [27] and mutagenic effects [28] and that NTA might be toxic for terrestrial and aquatic organisms [29-32]. Various other toxic negative effects have been mentioned [23].
A second drawback is the possibility that in sewage treatment under distinct circumstances the biodegradability of NTA may be insufficient. If the concentration of NTA in the waste water decreases the capacity of the sludge for the degradation decreases too and upon increase of the NTA-concentration re-adaptation is necessary [23, 33-35]. The consequence is that upon peak-loadings, occurring on washing days substantial amounts of NTA will be released into the environment.
The occurrence of NTA in surface waters is also possible because of the fact that at lower temperatures (< 10 °C) the rate of biodegradation diminishes considerably [22, 23, 35-37].
The influence of the water hardness on the rate of biodegradation has also been investigated [38, 39]. *Stoveland* et al. [38] found that NTA in the presence of activated sludge in soft water did not degrade within a period of 60 days, whereas in hard water acclimatisation was achieved within 16-30 days. On the other hand *Vashon* et al. [39]

observed biodegradation of NTA both in hard and soft water within 29 days. However, acclimatisation was achieved more slowly in soft water.

The biodegradability of NTA-complexes and the influence of water hardness have been investigated by several authors. Both *Björnland* et al. [40] and *Walker* [41] established that the biodegradation of the copper-NTA complex decreases upon decreasing water hardness.

Another matter of concern is that the occurrence of NTA in the environment may lead to remobilization of hazardous, heavy metals, which are adsorbed onto sludge [22, 23]. However, conclusive evidence does not seem available yet.

Despite these objections NTA is used in Canada in large quantities (36,000 tons/year). However, in most countries the use is limited by voluntary agreement or legislation [21]. In the Netherlands the consumption is estimated to be 100 tons /year, much less than the quantity allowed (6500 tons/year).

In other countries as Germany, Sweden and Switzerland the consumption is limited to < 1% (w/w) of the total detergent consumption.

Among the aminocarboxylic acids some other compounds are found e.g. the well-known ethylenediaminetetraacetic acid (EDTA, Fig. 3a) and HEDTA (hydroxyethyl-ethylenediaminetriacetic acid, Fig. 3b).

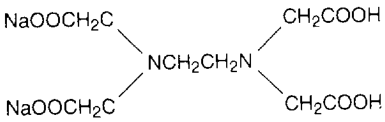


Fig. 3a. EDTA as disodium salt.

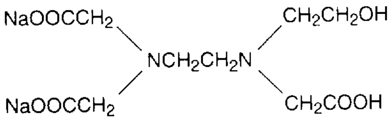


Fig. 3b. HEDTA as disodium salt.

These substances, used on a limited scale only, have excellent sequestering capacity for most metal ions (e.g. EDTA, log K_{Ca} = 11.6). They have been applied in small quantities in detergent formulations, mainly as stabilizer for bleaching agents by suppressing the catalytic activity of metal ions e.g. Fe(II). Because of the relatively high price and the poor biodegradability the compounds are not used as calcium and magnesium sequestering agents.

c. Hydroxycarboxylic acids

Many compounds containing carboxylate and hydroxyl groups have been synthesized and tested for their calcium and magnesium binding properties [16-18]. An important representative of this category is citric acid. In Europe this substance has been used in modest quantities, but in connection with liquid detergent formulation the use is increasing. Nowadays, especially in the USA, citric acid is used to a large extent. A drawback of this compound is that because of its relatively poor performance (log K_{Ca} = 3.8) large doses have to be applied, so that the biological oxygen demand of the discharged water is high.

The sequestering capacity of sugar acids has drawn attention in an early stage [42, 43]. It was shown that the borate esters of sugar acids were very promising. This subject will be discussed in more detail in this chapter.

In this group a few other representatives, which are in use as sequestering agent, are found: gluconic acid and tartaric acid. The performance of gluconic acid is only satisfactory at high pH [42].

d. Zeolite NaA

This material, an aluminosilicate ($Na_{12}[Al_{12}Si_{12}O_{48}].27H_2O$) [44, 45], exchanges its sodium ions to calcium and to a lesser extent to magnesium ions. It is a finely divided powder, consisting of cubic crystals with a typically particle diameter of 1-2 μm, which in water easily is suspended. The structure of the lattice and a model [46] are depicted in Fig. 4.

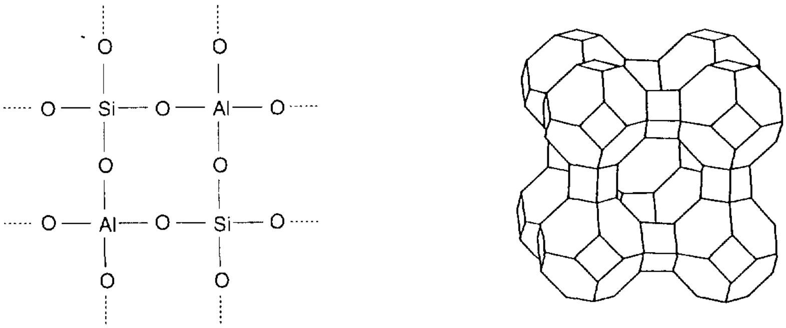


Fig. 4. The molecular structure and a model of zeolite NaA [46].

According to estimates the consumption of zeolite NaA in 1992 is 1,236,000 tons [47] A survey of the consumption in West-Europe, Asia and North-America is given in Fig. 5.

The properties with respect to calcium and magnesium binding and the eco-toxicological aspects have been discussed in numerous articles [23, 48-58].

The compound, an inorganic ion exchanger, is especially suitable for lowering calcium concentrations; the exchange of magnesium ions occurs slowly, which is due to the more strongly coordinated water [48, 57]. For an optimal prevention of incrustation

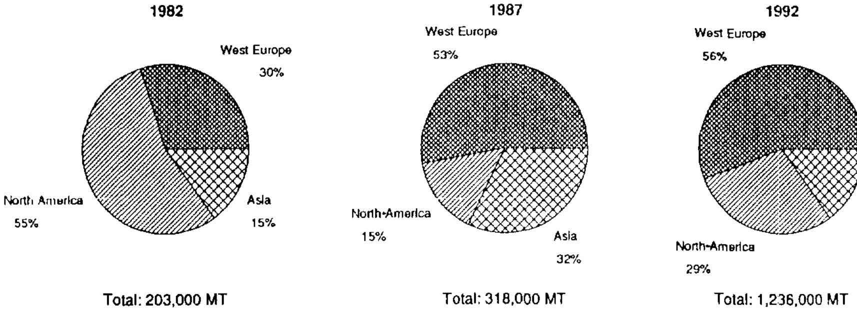


Fig. 5. The estimated consumption of zeolite NaA in West-Europe, Japan and North-America.

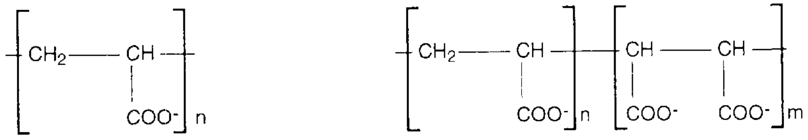
and washing action a water-soluble co-builder is desirable. On a molecular scale zeolite NaA particles are very large with the consequence that incrustations on the fabrics cannot be completely removed. The co-builder removes calcium and magnesium ions from the fabrics and transports these ions to the zeolite [50, 51, 58]. Examples are polycarboxylic acids (see below), citric acid [59] and sodium carbonate. Zeolite NaA is non-toxic both in aqueous environment and for humans and animals. Despite the distinct toxicological advantages of this substance several uncertainties remain about its safety. The removal in sewage sludge installations seems to be incomplete, mainly due to the small particles, which will not settle [23, 60, 61], resulting in the release of the compound into the environment. In zeolite NaA the aluminium is in principle a non-toxic constituent, because it is bound. It cannot be excluded however that hydrolysis of this compound may occur with the consequence that aluminium ions are released into the environment; a half-life of 1-2 months in neutral water has been reported [62].

Also concern has arisen about the fact that heavy metal ions may be remobilized in the environment. It has been shown that zeolite NaA has a positive effect on the removal of heavy metal ions from waste water. If, however, hydrolysis occurs the metal ions will set free. Also degradation of zeolite NaA in disposed sludge in the marine environment might lead to the release of these ions [23].

e. Polycarboxylates

A comprehensive review about polycarboxylates (or polycarboxylic acids-PCA) is given by *Hunter* et al. [63]. The subject is discussed in a more limited framework by *Dwyer* et al. [23] and *Floor* [21]. It appears that the use of polycarboxylic acids was already proposed long ago [64, 65]. They are nowadays used in modest quantities (1-5% by weight of the detergent formulation) as a co-builder in combination with

zeolite NaA. In this group several substances are commonly in use. Some of them are depicted in Fig. 6.
The function of these materials seems to depend on the molecular weight. Those with a relatively low molecular weight have water softening properties, whereas the high molecular weight products, because of their dispersing properties, also act as a crystal growth inhibitor [21, 23, 63].



Polyacrylate Copolymer of acrylate and maleate

Fig. 6. Examples of polycarboxylates.

The polycarboxylates generally are regarded as non-toxic, although it has been reported that some of them exhibit toxic properties; the toxicity may differ from substance to substance and strongly depends on the character of the polymer [66, 67]. It may be noted that several authors report antitumouric, antigenic, mutagenic and antiviral activities [63, 68].

The impact of the release of synthetic polycarboxylates into the environment is as yet difficult to estimate, because of the lack of analytical procedures for representatives of this class of compounds [23, 69]. The materials consist of polymers with different chain lengths and the matrix in which the material is present under environmental circumstances is complicated [23, 69].
Nevertheless there is strong evidence that the materials are not biodegradable or only to a slight extent [23, 63, 69, 70-73]. An exception is poly-(α-hydroxyacrylic) acid (PHAA). A ^{14}C labelled polymer appeared to degrade in a continuous activated sludge test [73]. Also other co- and homopolymers of this monomeric unit (α-hydroxyacrylic acid) seem to be biodegradable [23]. However, from the survey given by *Dwyer* et al. [23] it appears that most polycarboxylates have a low biodegradability. The fact that removal in sewage sludge installations is observed is probably due to precipitation or to adsorption onto clay materials [74, 75].
A few studies deal with the remobilization of heavy metals by polycarboxylates. Other ions than calcium and magnesium may be bound to a significant extent, but no evidence has been found for the remobilization of heavy metals from soil. It has been stressed that additional studies are highly desirable [23].

Potential new builders

A large number of carboxylate and ether group containing substances have been synthesized and tested for their calcium binding capacity [16-18]. As mentioned above only one compound is applied on a large scale (citric acid). Various other possibilities of which some representative examples follow below, have been considered.

a. Once a promising class of compounds were the oxidized mono- and disaccharides. As has been mentioned the behaviour of several sugar acids e.g. gluconic acid and glucaric acid have been investigated [42, 43], but it was found that such materials exhibit a satisfactory calcium binding capacity only at high pH (> 13). This value is too high for normal washing applications. A promising and interesting development was the use of saccharic acids combined with borate [76-78]. Especially glucaric acid drew attention because of its relatively good performance and the perspective that this compound can be prepared from the cheap glucose. Saccharic acids exhibit modest calcium binding properties, but these are greatly enhanced by the presence of borate at pH > 9, since under these conditions borate esters will be formed [76-78]. The best performing products are the borate esters of glucaric and idaric acid with a sequestering capacity of about 2 mmole Ca/g. However, recent studies have shown that at higher temperatures the sequestering capacity may be unsatisfactory, which makes this combination less attractive as builder in laundry detergents. Also considering the difficulties encountered with the production of these compounds [79] application of saccharic acids as builders does not seem to be feasible.

b. A particularly promising class of materials are the oxidized oligo- and polysaccharides. In a number of patents [80, 81] and papers [21, 82-87] it is described that selective oxidation of starch, cellulose and hemi-cellulose-containing substances leads to the formation of compounds which exhibit moderate to excellent calcium sequestering properties and indeed can be used as a phosphate replacer.
It has been recognized [16, 84, 88] that the calcium binding properties can be attributed to the presence of the oxy-diacetate structure (ODA), see Fig. 7 .

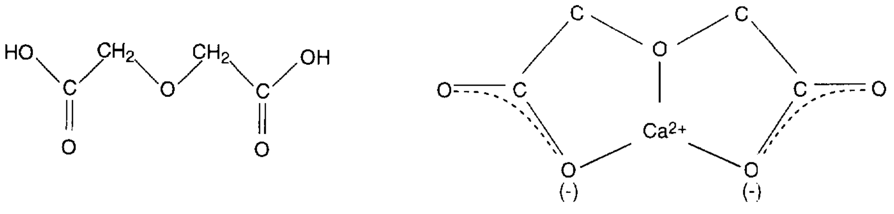


Fig. 7. Structure of ODA and its Ca-complex.

This structural feature coordinates calcium ions while adopting a W-shaped conformation. The ODA-moiety is found in starch and cellulose upon glycolic oxidation of two adjacent glucose units, see Fig. 8.

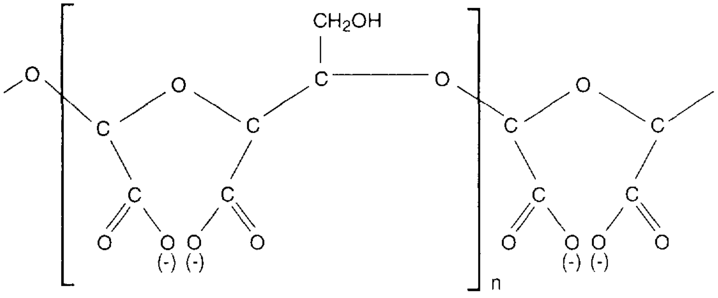


Fig. 8. ODA-moieties in oxidized starch and cellulose.

Methods for the preparation of calcium sequestering dicarboxypolysaccharides

A survey on the methods for the oxidation of starch has been given by *Radley* [89]. The feasible procedures for the preparation of dicarboxy-starch consist of oxidation with:

- sodium periodate followed by oxidation with sodium chlorite (denoted as process I)
- sodium hypochlorite (denoted as process II).

Also oxidation with Ag_2O, Pb(IV) and H_2O_2 has been mentioned.

Nieuwenhuizen et al. [84] advanced that the best sequestering products were obtained from the high molecular weight materials starch and cellulose (DP > 100) and to a somewhat lesser extent from the low molecular weight maltodextrins (DP = 10-50). It was established that for a satisfactory calcium binding a critical value was DP = 10. Cellulose yielded a somewhat lesser performing product than starch; oxidation of alginic acid afforded only a moderate sequestering agent, in spite of the presence of three carboxylic acid groups per unit. Inulin was reported to yield a relatively poor calcium sequestering agent. These authors concluded that starch is the most promising raw material. Their investigations were extended by *Floor* et al. [21, 85-87], who tried to find new preparation methods and improved the existing procedures. A survey of the characteristics of both processes is given in Table 1.

a. Process I

The advantages of the first process, the two step oxidation, are that the high-molecular weight of starch is retained and that a high oxidation degree is attained.

Both parameters are favourable for a good sequestering capacity. However, both the high-molecular weight and the high degree of oxidation (no natural units left) influence the biodegradability in a negative way. Further drawbacks are that expensive chemicals in large quantities are needed.

Table 1. Survey of expected properties and the costs of chemicals for the preparation of dicarboxy-starch by method I and II.

process	I. ($NaIO_4/NaClO_2$)	IIa. (NaOCl in excess)	IIb. (NaOCl stoichiometric)
product performance	good	moderate	moderate
prospects for biodegradability	bad	readily-inherently	readily-inherently
costs of chemicals	high-moderate[1]	moderate	cheap[2]

[1] *If the sodium periodate is regenerated electrochemically in situ.*

[2] *Especially an indirect electrochemical oxidation is favourable.*

The authors note that a reduction in costs will be achieved by carrying out the first step in such a way that the reaction product, sodium iodate, is regenerated electrochemically or with NaOCl [90-96]. In an electrochemical process the use of the expensive and dangerous $NaIO_4$ in large quantities is avoided because sodium iodate is regenerated *in situ*. The feasibility of this process has already been proven some forty years ago [91-97].

The second step of this process consists of the oxidation of dialdehyde starch with $NaClO_2$ which requires 6 moles, being much more than the stoichiometric amount (2 moles). This is due to the fact that HOCl arises, which decomposes $NaClO_2$.

$$HOCl + 2\,ClO_2^- \rightarrow 2\,ClO_2 + Cl^- + OH^-$$

The use of 2 moles H_2O_2 [87] reduces the amount of $NaClO_2$ to two moles.

$$HOCl + H_2O_2 \rightarrow HCl + H_2O + O_2$$

Other advantages of this procedure are the improvement of the quality of the products, resulting in a somewhat higher sequestering capacity than the products obtained via the conventional procedure and a somewhat higher yield.
Despite these improvements a relatively high price is expected, mainly due to the price of sodium chlorite.

b. Process II

The performance of the products, obtained by the hypochlorite oxidation, is reported to be distinctly less than that obtained via process I. Two reasons are responsible:

- the products have a lower degree of oxidation
- due to the oxidation at the C-1 atom depolymerization occurs.

An advantage is that the material will be cheaper since sodium hypochlorite is a relatively cheap agent.
With reference to the sodium hypochlorite oxidation three major problems had to be solved.

1. The amount of NaOCl, needed for the complete oxidation, seemed to be higher than the theoretical amount of 3 moles [80-82, 84], (carried out in this way the method is denoted as Process IIa, see Table 1).

2. The oxidation has to be carried out at $pH > 8$ in order to suppress the formation of sodium chlorate. For practical reasons the reaction rate may be too low at this pH i.e. a reaction time of 2-3 days is expected [21, 86].

3. A serious drawback is the fact that the products obtained by this method are coloured, which is undesirable for detergent formulations [84]. This may be attributed to the formation of materials which contain carbonyl functions [97, 98]. The process should be changed in such a way that the formation of precursors of coloured products is prevented. Possibilities for improvements have been discussed by *Prey* et al. [98].

A general objection (in both procedures) is formation of large amounts of NaCl, which have to be separated and discharged.
It appeared from the study of *Floor* et al. [86] that the procedure could be improved by several means. By the use of the stoichiometric amount of NaOCl (denoted as Process IIb.) reasonable performing products were obtained. Our investigations show the possibilities for improvements of the sodium hypochlorite oxidation by using bromide as a catalyst [99, 100]. Results of this study will be reported in this thesis.

Survey of the hypochlorite oxidation of polysaccharides

The oxidation of starch with sodium hypochlorite has been used for many years with the objective to prepare the so-called thin boiling starches. Surveys on this subject have been given by *Radley* [89] and by *Ruthenberg* and *Solarek* [101]. Only modest amounts of hypochlorite leading to just partial oxidation are used for this application (1-5%).
The complete oxidation of starch with NaOCl for the preparation of calcium complexing agents was initially carried out with a threefold excess of this reagent [80-82]. The performance of the products obtained in this way seemed to be equivalent to that of STP in washing experiments [80, 81]. Also the sequestering capacity was equal [82]; however, it should be stressed that these experiments are not representative for the more quantitative approach by *Nieuwenhuizen* et al. [84] and *Floor* et al. [86, 87], who characterized the products by measuring the (intrinsic) complex constant and the calcium sequestering capacity and by carrying out a conformational analysis of the product.

With respect to the NaOCl-oxidation many studies have been carried out covering the following aspects, which are important for the as complete as possible oxidation of starch:

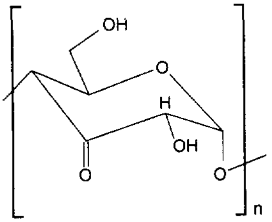
- product formation
- mechanism
- kinetics
- catalysts
- properties.

Product formation

Although the first reliable results of the complete hypochlorite oxidation of polysaccharides (starch and alginic acid) were published 40 years ago by *Whistler* and co-workers [102-105], there remains a controversy about the products formed. *Boruch* [106] states that hypochlorite oxidation yields primarily glucuronic acid polymers (6-CH_2OH oxidation). The final answer seems to have been given by *Floor* et al. [86] who confirmed that 2,3-dicarboxy-starch is the most important product, in agreement with the results described by *Whistler* and co-workers. Both *Whistler* et al. and *Floor* et al. found that the hypochlorite oxidized starch after hydrolysis yielded mainly glyoxylic acid and erythronic acid. These results indicate unambiguously 2,3-oxidation.
A few authors have studied the influence of the pH on the product formation. One of the most important conclusions is that below pH 4 the formation of polyglucuronic acid is enhanced [102, 104, 107].

Mechanism

So far no detailed studies seem to exist regarding the character of the intermediates. It has been recognized that carbonyl compounds [97, 98] may be formed, but the structure has not been elucidated. The following structure is a plausible intermediate:



The character of the intermediates and their reactivity may explain the formation of coloured by-products.

Kinetics

In view of the dissociation of hypochlorous acid the rate of the oxidation of starch and cellulose with this reagent will be pH dependent. *Whistler* and co-workers have found that the highest oxidation rate is found at pH 7 or slightly higher [102]. Moreover they established that at low and high pH the rate is significantly lower than at pH 5-7.
Kinetic studies have been carried out by *Patel* et al. [108, 109] and by *Schmorak* et al. [110]. *Patel* et al. investigated the rate of the hypochlorite oxidation in the region between pH 4 and 10 (with intervals of 1.5 pH units); the highest reaction rate was at pH 7. *Schmorak* et al. determined the rate constants between 7.5 and 11 and found the highest rate at pH 7.5. Regrettably lower pH values were not considered by them.
The studies directed to the oxidation of cellulose confirm these results, namely that the highest rate occurs approximately at pH 7 [111-113].
In view of the dissociation of hypochlorous acid at high pH (>7) and the chlorine formation at pH < 4 one may conclude that neither HOCl nor OCl^- are the active species involved in the oxidation [111-113]. In Fig. 9 the (relative) concentrations of HOCl, OCl^- and chlorine are given as a function of pH.

Hence, it is plausible that one or more reactive intermediates arise from a reaction in which both OCl^- and HOCl are involved and that these species are responsible for the oxidation of starch [111-113]. Various mechanisms and reactive species have been postulated: chlorine and oxygen atoms and ClO- and OH-radicals. The exact mechanism is not clear as yet.

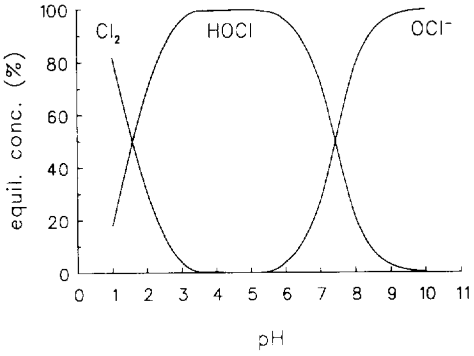


Fig. 9. The relative distribution of chlorine, hypochlorous acid and hypochlorite as a function of pH at 20 °C.

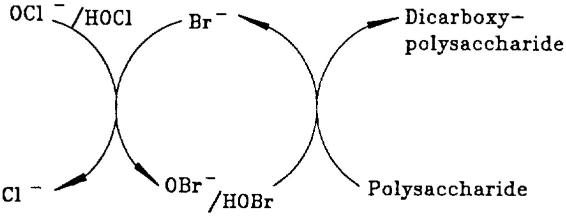
Catalysts

It has been shown that the reaction rate may be increased by catalysts. Two categories have been studied.
The first one concerns metal ions: cobalt, copper, manganese and iron salts were found to be active as a catalyst. Generally these metal ions can catalyze (i) the carbohydrate oxidation (ii) the decomposition of the hypochlorite (towards chlorate). Obviously the latter reaction is not desired.

In cellulose chemistry i.e. bleaching of cotton, the catalytic effect of various metal ions has been studied [114, 115]. Cobalt salts proved to be the most effective. The catalytic effect of various other metal ions has also been investigated in the starch oxidation [116]. Here, it was reported that the use of cobalt salts led to two improvements:

- a higher reaction rate
- a higher content of carboxylate groups in the product.

A second catalyst is bromide, which has been used in the partial oxidation of starch [116]. It appears from various investigations that hypo-bromite reacts faster with glycolic systems than hypochlorite [116, 118, 119]. Characteristic for this reaction is that the optimal reaction conditions are found at higher pH. *Doane* and *Whistler* [118] found that the optimum is at pH 9; the highest rate occurs at this pH and the highest number of carboxylic groups is introduced. A similar result is obtained by *Potze* and *Hiemstra* [116], who investigated the influence of catalysts like cobalt, bromide and the combined action of these substances in the hypochlorite oxidation of starch. A shift in the pH optimum from 8 to 9 is observed, the amount of carboxylate groups increases as well as the reaction rate. The role of bromide is based on the fast conversion of hypochlorite into hypobromite [117], which reacts faster than hypochlorite. A scheme for the reaction is given below.



Floor et al. [88] explored the influence of bromide and of cobalt/bromide as catalyst in the complete oxidation of starch with sodium hypochlorite. In the presence of cobalt salts and bromide the reaction rate increased only slightly. These authors also observed that depolymerization is an important side reaction and that the product obtained in this way has a lower performance. Upon oxidation with bromide as the sole catalyst the properties of the products were very similar to those of the products of the non-catalyzed reaction, but the yield was lower. However, a comparison of these results and those by *Potze* and *Hiemstra* makes clear that the relative amount of bromide used by *Floor* with respect to the oxidizing agent is rather small. From the rate constants for the oxidation with hypochlorite [108-110] and hypobromite [119] it follows that hardly any effect could be observed. A survey of the rate constants is presented in Table 2. It has to be noted that the respective authors measured the consumption of the oxidant (OCl^-,OBr^- respectively) as a function of time and derived from the data the first-order rate constant (k_1). According to the data given by *Schmorak* et al. [110] the second-order rate constant (k_2) of the reaction

$$\text{starch} + OCl^-/HOCl \rightarrow \text{products}$$

was found to be 0.006 M^{-1}. min^{-1} (pH 8.5-9).

In *Floor's* experiments the $HOCl/OCl^-$ consumption due to the reaction of starch with $HOCl/OCl^-$ at $C_{starch} = 0.25$ M and $C_{NaOCl} = 0.75$ M is given by

$$-d[HOCl]/dt = k.C_{HOCl} \cdot C_{starch} \quad (= 1.1\ 10^{-3} M.\ min^{-1}).$$

The second-order rate constant of the $Br_2/HOBr/OBr^-$ oxidation [1] is estimated to be 0.13 $M^{-1}.min^{-1}$. Then the contribution to the $HOCl/OCl^-$ consumption due to the presence of the catalyst at $C_{bromide}$ = 0.002 M (as used by *Floor)* is given by

$$-d[HOCl]/dt = k.C_{HOBr} \cdot C_{starch} \quad (= 6.5\ .10^{-5} M.\ min^{-1}).^{2}$$

This contribution to the overall reaction rate is about 6% and is too small to be observed.

Table 2. Rate constants of the oxidation of starch in water with halogen/hypohalous acid/hypohalite at 300-303 K.

Oxidant[1]	pH	$k_1 \times 10^3 (min^{-1})$ [2]	$k_2 (M^{-1}.min^{-1})$ [3]	Ref.
$HOCl/OCl^-$	7.5	3.15	0.018	110
	8.0	2.67	0.015	
	8.7	1.20	0.007	
	9.0	0.98	0.006	
	10.0	0.42	0.002	
	11.0	0.40	0.002	
$HOCl/OCl^-$	4.0	5.4	0.009	108, 109
	5.5	4.8	0.008	
	7.0	13.2	0.022	
	8.5	7.8	0.013	
	10.0	4.5	0.007	
$HOBr/OBr^-$	6.0	1.95	0.059	119
	7.0	2.18	0.066	
	8.0	2.49	0.075	

1 Concentration starch 0.175, 0.6 and 0.033 M, respectively for upper, middle and bottom part of the Table.

2 Pseudo-first-order rate constant (starch in excess).

3 Second-order rate constant.

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[1] By extrapolation of the results of *Ziderman* and *Bel-Ayche* [119], who carried out experiments at pH 8.0 and 30° C.

[2] Because the reaction between OCl^- and Br^- is fast [117] C_{HOBr/OBr^-} is constant.

Properties of dicarboxy-polysaccharides

An important property of dicarboxy-starch is its calcium binding capacity. As mentioned above, it has been shown that in detergent formulations dicarboxy-starch may replace sodium tripolyphosphate (STP) [80, 81]. This conclusion was based on the results of standard washing experiments. Contaminated fabrics were washed with a standard detergent containing STP and dicarboxy-starch as builder, respectively. The removal of the dirt was compared by measurement of the brightness of the fabrics; details about the extent of incrustation have not been published in these patents. From measurements by *Nieuwenhuizen* et al. [84] and *Floor* et al. [87] follows that the calcium sequestering capacity may be equal to or even exceeds that of STP. The sequestering capacity of the products prepared by hypochlorite oxidation of starch is generally inferior to that of the materials prepared via the two-step procedure [21, 86, 87].

Floor et al. also showed that after hypochlorite oxidation with a stoichiometric amount a subsequent re-oxidation yielded a product with a lower degree of polymerization but a considerably higher sequestering capacity and carboxylate content. These results can be explained by assuming that the first oxidation was incomplete, owing to the formation of chlorate. In chapter 6 of this thesis this matter will be discussed in more detail.

Dicarboxy-inulin as calcium sequestering agent

So far only the glucans starch and cellulose seemed to be promising as raw material for the preparation of calcium binding agents.

Contrary to the expectation the fructan inulin, oxidized via the two-step procedure was reported not to yield a material with a high sequestering capacity [84]. As discussed above the calcium binding properties of oxidized glucans have to be attributed to the multiple occurrence of the ODA-structure, requiring neighbouring oxidized glucose units *cf.* Figure 8.

In inulin (Fig. 10) the ODA-structure is obtained directly for each fructose unit upon glycolic oxidation (Fig. 11).

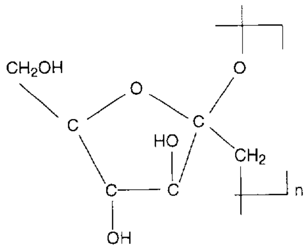

Fig. 10. Structure of inulin (the upper terminal unit is glucose).

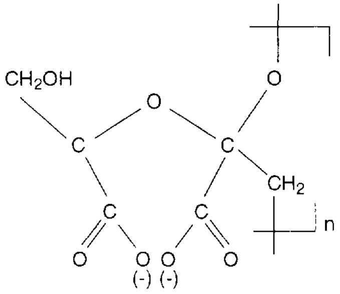

Fig. 11. The multiple occurrence of ODA-units in oxidized inulin.

One may therefore expect that oxidized inulin will be a good calcium binding agent. So far this hypothesis could not be confirmed, due to the lack of a suitable preparation method. As mentioned above two methods are available for the oxidation of the vicinal diolgroups in carbohydrates. The products which were obtained from inulin by consecutive oxidation with sodium periodate and sodium chlorite had only a poor calcium binding capacity [84]. *Floor* [120], using the improved method of this procedure, obtained similar results. A possible explanation for these disappointing results is the formation of relatively stable hemi-acetals in the first oxidation step, which is carried out in slightly acidic medium. It is known that in the so-called dialdehyde starch practically no aldehyde groups are found: the material mainly contains inter and intra hemi-acetal groups. In the second step it is necessary that hydrolysis occurs before oxidation takes place. If hydrolysis of the dialdehyde inulin in the second step is slow, the oxidation with sodium chlorite will be retarded and exceptionally long reaction times will be required. *Floor* et al. and *Nieuwenhuizen* et al. did not investigate these aspects.

In order to avoid the formation of acetals or ketals the oxidation has to be carried out in neutral or alkaline medium. The second procedure, oxidation with NaOCl, may therefore be more suitable, because the reaction conditions are alkaline (pH between 7 and 10). This could be confirmed by us after some exploratory experiments [100]. Details will be presented in chapter 3 of this thesis.

Scope of this thesis

From the survey given above it is clear that many questions about the hypochlorite reaction and the relation between calcium sequestering properties and the character of the oxidized carbohydrates remain. In this thesis our investigations concerning the hypochlorite oxidation of carbohydrates are described. The objectives were as follows:

1. to elucidate the mechanism of the hypochlorite/hypochlorous acid oxidation of carbohydrates and to establish the kinetics of the hypochlorite oxidation with and without catalysts

2. to extend the oxidation to other carbohydrates than starch with special emphasis on inulin being a promising renewable raw material, which will be available on a large scale

3. to characterize and compare the products which are obtained from starch and inulin

4. to study the structure of the calcium complexes of dicarboxy-inulin

5. to optimize the reaction conditions for the production of oxidized carbohydrates from starch and inulin

6. to optimize the reaction conditions in order to obtain products which are biodegradable while having a good performance as a (co-)builder

7. to obtain evidence about the possibility and feasibility of the indirect electrochemical oxidation.

If dicarboxy-starch or dicarboxy-inulin is satisfying as co-builder some important aspects and parameters should be considered:

- the biodegradability
- the expected costs of the product
- the environmental impact of the product and its manufacture.

The biodegradability is probably related to (i) the molecular weight and (ii) the degree of oxidation. Dicarboxy-maltodextrins seem to be readily degradable whereas dicarboxy-starch is difficult to degrade [82]. Apparently one has to look for a compromise: a lower molecular weight product with a somewhat lower performance but being biodegradable. The biodegradability is probably a parameter which has to be established by empirical means i.e. if the rate of degradation is (too) slow the reaction conditions have to be altered in such a way that either more depolymerization of the starch during the oxidation occurs or a lower number of carboxylate groups is introduced.

It appears from the introduction above that the hypochlorite oxidation in an economical sense is the most attractive way to prepare dicarboxy-starch and dicarboxy-inulin. The

depolymerization might therefore be advantageous[1]. However, there remain various problems connected with this route, which have to be solved before an economical process for the preparation of an environmentally safe product can be introduced. Beside the biodegradability the expected costs of the new product are of importance. From a simple survey of the costs and on basis of several assumptions, it may be shown that the price of dicarboxy-starch will be approximately the same as that of synthetic polycarboxylates. It can be calculated that to a large extent the price of dicarboxy-starch is determined by the costs of the oxidant. Because of the higher price of inulin this material is expected to contribute significantly to the over-all price. As stated above bulk production of inulin has started, which undoubtedly will lower its price.
Finally the salt burden should be considered in connection with the environmental impact.

The cost aspects and the environmental consequences of the processes, directed to the production of both dicarboxy-starch and dicarboxy-inulin will be discussed in chapter 8.

As already mentioned a bromide-catalyzed reaction offers several advantages [99, 100], because this method allows the preparation via an indirect electrochemical process.
In various papers the indirect electrochemical oxidation of carbohydrates with alkaline hypochlorite or bromine/hypobromite has been discussed [121-123]. In such a process the salt burden is limited because only a relatively small amount of sodium bromide is needed: the bromide in alkaline medium is oxidized to hypobromite, reacting with the substrate, resulting in the formation of a product and bromide. The latter material will be recycled electrochemically. Also the costs will be reduced as the costs for the regeneration of hypobromite are lower than the costs of the hypochlorite reagent. A further advantage is that dilution is minimized, which limits the energy costs for down-stream processing.

The adaptation of a laboratory method to an indirect electrochemical process needs a fundamental and detailed knowledge about mechanism, kinetics and reaction conditions. This thesis deals with the fundamentals of some of the processes mentioned above.

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[1] Mild hydrolysis of the reaction products obtained via route I. will lead to a lower molecular weight and therefore probably to a better biodegradable material. A third step in this process is however a further draw-back.

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CHAPTER 2

OXIDATION OF STARCH WITH SODIUM HYPOCHLORITE IN THE PRESENCE OF BROMIDE

Summary

Various aspects of the glycolic oxidation of the glucose-units of starch with stoichiometric amounts of sodium hypochlorite and sodium bromide as the catalyst have been investigated. The main objective of the study was to optimize the reaction conditions for the preparation of the product (dicarboxy-starch) and to establish the calcium sequestering capacity of the material.

The products, polycarboxylates, are obtained in high yields (90-95%) and they have a sequestering capacity up to 1.4 mmole Ca/g, which is somewhat higher than that of the materials obtained in a non-catalyzed hypochlorite oxidation. This result is attributed to the fact that the reaction with sodium bromide may be carried out at higher pH (> 9) than the non-catalyzed reaction and that a relatively low concentration of hypochlorite throughout the process could be maintained. In this way the decomposition of hypochlorous acid/hypochlorite, especially occurring at high concentration of hypochlorous acid at lower pH (6-8) is prevented.

Other advantages of this procedure are the colourless appearance of the materials and the higher reaction rate. The feasibility for large-scale preparation follows from the results of a few exploratory experiments, including an electrochemical preparation.

Introduction

It is well-known that the use of sodium tripolyphosphate (STP) in detergent formulations as calcium and magnesium sequestering agent is subject to regulations because it leads to eutrophication of surface waters including lakes and seas [1-10]. For this reason extensive studies have been carried out with the aim to find an alternative for STP which meets all requirements. The main demands of such substitutes are:

- good performance (Ca- and Mg-binding)
- good biodegradability/biocompatibility
- low price
- preferentially good soluble in water, but not hygroscopic
- non-toxic.

A nowadays commonly used alternative for STP is zeolite NaA [11-22], which has several attractive properties: it is cheap (NLG 1.00-1.50 /kg), the calcium binding is satisfactory, and the substance is non-toxic. The estimated world production of detergent zeolite NaA amounted to 1,236,000 tons in 1992 [23]. However, there are also some drawbacks involved in the use, namely the non-water solubility and the slow binding of magnesium ions, especially at lower washing temperature [12, 24]. Moreover deposits (incrustations) formed on the fabrics during the washing process do not dissolve. In view of these aspects a so-called co-builder is added, which prevents the formation of incrustation and functions as a carrier, transporting the calcium and magnesium ions to the zeolite NaA [20, 21]. Polyacrylate and copolymers of acrylate and maleate are widely used for this purpose, but because of their non-biodegradability the application of these material is also under discussion [25].

Since it has been recognized that oxidized starch possesses good calcium binding properties and as a consequence may be applicable as a substitute for STP, a number of studies have been carried out in order to evaluate this type of synthetic polycarboxylate [26-33]. The advantages of starch are the low price and the renewable character. In some early studies only the possibility of phosphate replacement was considered [26-28]. It was found that the performance was satisfactory, but the costs of application in detergent formulations would be probably too high, due to the expensive oxidation method and the large amounts needed for a good performance.

It seemed therefore better to apply dicarboxy-starch as a co-builder, as proposed by *Nieuwenhuizen* et al. [29]. From a series of studies in which several preparation methods have been investigated thoroughly, *Van Bekkum* and *Kieboom*, and co-workers [29-33] concluded that two methods are promising.

The first method is a two step procedure consisting of consecutive oxidation with sodium periodate and sodium chlorite [29, 32, 33].

In one of the most recent studies on this method carried out by *Floor* et al. [30-33] it was confirmed that the best products were obtained in the two-step procedure, as was found by *Nieuwenhuizen* et al. The better performance of the products obtained via this method is attributable to the retention of the high molecular weight and the fact that more carboxylate groups are introduced in the molecule. An important improvement was obtained by using hydrogen peroxide in the second step. The net effect is a much lower consumption of the relatively expensive sodium chlorite (2 moles per mole glucose-unit instead of 6 moles), a somewhat higher yield and better performing products. The disadvantages are that the process has to be carried out in two steps and that relatively expensive reagents as sodium periodate and sodium chlorite are needed. Moreover the high molecular weight starch-based polycarboxylates may be less biodegradable[1] [28].

The second procedure is a one-step conversion: oxidation with sodium hypochlorite [31]. Although *Boruch* states [39] that oxidation at the 6-position of the glucose-unit occurs, there is little doubt that the reaction proceeds as described by *Floor* et al. In a series of studies *Whistler* and co-workers [34-37] have proven that 2,3-scission occurs resulting in the formation of dicarboxy-starch. These results are confirmed by the studies of *Kohn* [38] and *Floor* et al. [31]. Additional evidence originates from older literature, in which it is stated that in acidic medium oxidation at the 6-position occurs, whereas in alkaline medium oxidation at the 2,3-position prevails [34, 40].
Advantages of this method are that sodium hypochlorite is relatively cheap, that the oxidation can be carried out in one step and that some depolymerization occurs, which gives better prospects for the biodegradability of the product.
The sodium hypochlorite oxidation has also several drawbacks.

1. For the production of 1 mole of dicarboxy-starch (as glucose-unit) theoretically 3 moles of sodium hypochlorite are needed and consequently 3 moles of NaCl will be formed. Because of environmental legislation the discharge of NaCl will lead to extra costs. It may be noted that - in principle - electrochemical regeneration of chlorine and hypochlorite *in situ* is possible.

2. The products obtained in this way are coloured [29, 31], which may be undesirable for use in detergent formulations.

3. The price of dicarboxy-starch may be too high, despite the fact that relatively cheap reagents are used.

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[1] It seems not difficult to hydrolyse [33] the high molecular weight products in order to obtain biodegradable materials. The hydrolysis can be carried out before or after oxidation. Of course this will have consequences for the costs of the product.

It is known that the oxidation rate of starch and of cellulose with sodium hypochlorite can be increased by catalysts like salts of cobalt and nickel and bromide [41-44]. The role of the latter compound is ascribed to the fast conversion into hypobromite [45], which reacts faster than hypochlorite and at higher pH [41, 46] which may have some advantages. *Potze* and *Hiemstra* [41] have found that the reaction of starch with hypochlorite in the presence of one these catalysts leads to the formation of products with a lower carbonyl content and a higher carboxylate content, which will enhance the sequestering capacity. Contrary to these results *Floor* et al. [31] found no beneficial effect of the use of bromide in some exploratory experiments [1]. However, it is evident from the literature that the rate of the oxidation of starch with hypobromite/hypobromous acid is substantially higher than that of the reaction with sodium hypochlorite/hypochlorous acid [46, 47]. The disappointing results of *Floor* may be attributed to the low catalyst concentration. Apparently, there is a need for further research regarding this subject.

For these reasons various possibilities for improvement of the whole oxidation process have been studied and found by us [48]. By gradual addition of the hypochlorous acid/hypochlorite solution high concentrations of this reagent are avoided and herewith the decomposition of the reagent. Apparently, a more efficient use of the oxidant is achieved in this way. It appeared that via this procedure white to very light yellow products were obtained, with satisfactory properties. As expected the most pronounced improvement was achieved by using bromide as catalyst [48]. Prerequisite was the use of *substantial amounts* of this catalyst. Despite the low $HOCl/OCl^-$ concentration, maintained throughout the reaction, a high reaction rate is obtained. In this chapter the results are presented of our study on the bromide-catalyzed oxidation of starch with sodium hypochlorite. Special emphasis was put on the influence of the reaction conditions on yield and calcium binding properties of the products.

In view of the possibility that in the future a large-scale preparation will be carried out, we have studied in a limited programme the feasibility of two methods.

The main problem in the classical route is the separation of the large amount of NaCl produced (about 700g /kg dicarboxy-starch). Ultra- or nanofiltration offers the possibility to separate these substances in a simple and cheap way. The feasibility of this procedure has also been investigated by us and the results will be reported.

An alternative for large-scale production is an indirect electrochemical process[2]. Starch is oxidized in an electrochemical cell in the presence of a small (catalytic) amount of hypobromite. The bromide formed after oxidation is regenerated at the anode, so that

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[1] The amount of catalyst used by *Floor* et al. was relatively low: 0.008 mole NaBr/mole starch corresponding to 0.0027 mole NaBr/mole NaOCl). *Potze* and *Hiemstra* used a 0.125 - 0.0125 NaBr/NaOCl molar ratio.

[2] The feasibility of this procedure follows from a procedure for the preparation of gluconic acid from glucose [49].

the salt burden may be limited. In this chapter an example of a large scale preparation will be described.

Experimental

Materials

The following materials were used:

- waxy maize starch (ZBB de Bijenkorf, The Netherlands)
- wheat starch (gift from Latenstein, Nijmegen, the Netherlands); protein content < 0.25%
- Promozyme (NOVO)
- NaOCl-solution (100 g of Cl_2 dissolved in 1 liter demineralized water containing 0.3 % excess NaOH for stabilization)
- NaOH-solution (Merck)
- HCl-solution (Merck)
- $CaCl_2$ (Merck p.a.)
- NaBr (Merck p.a.)
- methanol (Merck p.a.)
- ethanol (Gist-brocades)
- linear and maltodextrins.

Linear dextrins (amylodextrins) were prepared from waxy maize starch following a procedure described in the literature [50]. Waxy maize starch (8%) was gelatinized at 100 °C in water and after cooling to 55 °C the suspension was incubated with pullulanase (Promozyme, NOVO) at this temperature and pH 5, resulting in specific hydrolysis of the α-1,6 bonds. The average degree of polymerization (DP) of the dextrins was characterized by measuring the reducing capacity [51] and the total carbohydrate content [52] of the product (the average DP = 25). It was shown by HPLC-GPC [53] that the products have a bi-modal distribution; 75% consists of a fraction DP = 15-45 and 25% of DP = 45-75.
Maltodextrins were prepared from wheat starch by hydrolysis of gelatinized starch with 10^{-3} M HCl at 95 °C, during respectively 3, 3.5 and 4.5 hrs. The average DP was determined as described above (linear dextrins). For the three batches was found DP = 85, 50, and 25, respectively.

Methods

The calcium binding capacity of the products was determined by using a Ca-ion selective electrode (Radiometer F2002) in combination with a calomel electrode (Radiometer, K

401). For the calibration of the electrode aqueous solutions of 10^{-2}, 10^{-3}, 10^{-4}, 10^{-5} and 10^{-6} M $CaCl_2$ were used. The calibration curve (log U vs. C $_{Ca(II)}$) was linear in the region between 10^{-2} to 10^{-5} M, according to the specification of the supplier. Below these concentrations the electrode was less sensitive, but reproducible measurements could be carried out down to 10^{-8} M $CaCl_2$, provided in the solution NaCl (5.10^{-3} M) was present and the solutions were stirred well in a reproducible way.
The sequestering capacity (SC) was measured by titration as follows: small amounts (10-20 mg) of dicarboxy-starch were added subsequently to 100 ml of an aqueous 10^{-3}M $CaCl_2$ solution. After 2 minutes of stirring the resulting Ca(II) concentration was measured. The pH was kept between 10 and 10.3. From the titration curve (see Fig. 1) the amount needed for lowering the concentration to 10^{-5} M Ca(II) was found by interpolation. The calcium sequestering capacity is defined as the number of mmole Ca(II), that is coordinated by one gram of the sequestering agent at pH 10-10.5 until the concentration of non-bound Ca(II) is 10^{-5} M. This value is considered to be the upper limit in the washing process at which no incrustation occurs.

Preparation of dicarboxy-starch as disodium salt (small scale)

The preparation of dicarboxy-starch on a 2-5 g scale was carried out in a double-wall vessel (volume 150 ml), provided with an inlet for NaOH dosage, and a combined pH glass electrode. In the first and second series of experiments 5 g of dextrins or starch was dissolved in 50 ml, respectively suspended in 25 ml water, and cooled to the desired temperature. To the stirred reaction mixture a known amount of sodium bromide was added, followed by a small amount (3-5 ml) of the sodium hypochlorite solution. After an initial sharp raise of the pH (11-11.5), a fast decline was observed attributable to acid formation. The total amount of NaOCl was added in the course of 6-8 hours (unless otherwise indicated). The pH was kept constant by adding NaOH-solution, controlled by a pH stat. By heating the reaction mixture at 40-45 °C (after about 50% conversion) the oxidation could be completed within one day (this procedure concerns the experiments mentioned in Table 2). The reaction mixture (about 150 ml) was concentrated to about 50 ml and poured into 150 ml well-stirred ethanol. After standing for one day a white solid/oily precipitate was obtained from which the solution was decanted. The residue was dissolved in 50 ml water and poured slowly and gradually into 150 ml well-stirred absolute methanol. After standing for one day at 6 °C the solid precipitate was collected on a glass filter, washed two times with absolute methanol and dried in vacuum at 50 °C to yield the sodium starch dicarboxylate. Additional experimental details are given in the paragraph Results.

The conversion of the 100-150 g samples was carried out in 5 l Erlenmeyer flasks. The contents were stirred magnetically. Provisions were present for NaOH- and NaOCl-addition and pH measurement and control. The preparation and isolation were carried out in a similar way as the small-scale preparations described above.

Preparation of dicarboxy-starch (large scale)

The preparation of about 5 kg of dicarboxy-starch was carried out in a stainless steel 100 l vessel. The vessel was provided with a mechanical stirrer, a (combined) pH glass electrode and inlets for dosage of sodium hypochlorite and sodium hydroxide solutions. Starch (4.4 kg of dry material, 27 mole glucose units) was suspended in 15 l of water. In the course of 6 hours 60 l of sodium hypochlorite solution (85 mole) was added. The pH was kept at 9.5, controlled by a pH-stat (Metrohm). After 20 hours reaction the temperature of the mixture was gradually raised to about 40 °C and kept at this temperature during 10 hours. The reaction mixture was concentrated and desalted using a membrane process. The membrane was a hollow-fibre type, (HF1-43PM2) with a surface area of $0.288 m^2$. The flux with demi-water was 1 $l.h^{-1}$ at 2 bar. With the product the flux was 1 $l.hr^{-1}$, decreasing gradually to 0.7 $l.hr^{-1}$. The reaction mixture (about 100 l) was concentrated to about 20 l. The solution was diluted with 5 l water and concentrated again. The procedure was repeated several times until the conductivity of the solution did not change anymore, indicating that NaCl and NaBr were completely removed. Finally, the resulting solution was concentrated to a volume of 12 l, and freeze-dried to yield 5.6 kg of disodium starch-dicarboxylate.

Exploratory preparation of dicarboxy-starch via an indirect electrochemical process

The electrochemical preparation had an exploratory character. The electrochemical cell was a tube, length 40 cm, diameter 10 cm, with a volume of about 3 l. The platinized titanium electrodes were placed vertically. The effective surface area of the anodes was 150 cm^2. The cathodes were of the same material and were placed between the anodes. The cell voltage was maintained at 3.5-4 V, leading to a current of 100 A.
In 6 litre of water 100 g of NaBr was dissolved and 200 g of starch was suspended. This mixture was recirculated through the electrochemical reactor. Despite the ice cooling the reaction temperature was relatively high: 17 °C. The pH was kept between 9.8 and 10.2 by addition of NaOH. After approximately one hour the starch was completely dissolved. During approximately 6-8 hours current was led through the cell. Based on the consumption of NaOH the oxidation degree was 80%. The dicarboxy-starch was isolated by precipitation of the aqueous solution in alcohol. After dissolving the precipitate in water the procedure was repeated. The solid material was collected by filtration and dried. The yield was 80%; the sequestering capacity of the product was 1.0 mmole Ca/g.

Determination of the degree of oxidation and of the yield

A known amount of the substance was converted into the acid form by ion exchange (Amberlite IR120, H^+ form). The solution was freeze-dried, herewith removing water and the (volatile) acids HCl and HBr. Based on weight the percentage of dicarboxy-starch was determined. The samples were dissolved in water and titrated with 0.2 M sodium hydroxide solution to determine the carboxylic acid content.

Results

a. The partial oxidation of dextrins

The results of these experiments are summarized in Table 1.

Table 1. The (incomplete) oxidation of malto- and linear dextrins with sodium hypochlorite and bromide as catalyst.

Exp.[1]	Substrate	pH	Br^-(%)[2]	NaOCl (% of theoretical amount)	Y [3](%)	SC (mmole Ca/g)
1	MD (1)	9.0	1	55	56	0.4
2	MD (2)	9.0	1	55	60	0.6
3	MD (3)	9.0	5	55	65	0.6
4	LD	9.0	5	60	80	0.5
5	LD	8.7-9.3	5	55	73	0.5
6	LD	8.2-8.8	5	120	84	0.7

[1] *Abbreviations: MD = maltodextrins (exp. 1 average DP = 25, exp. 2. DP = 50, exp. 3. DP = 85). LD = linear dextrins; SC = sequestering capacity.*
Conditions: experiments 1-3 initial temperature 10 °C; experiments 4-6 15-20 °C.

[2] *w/w starch. The initial concentration Br^- was approximately 0.01- 0.05 M.*

[3] *Yield (Y) is based on M = 162 for an anhydroglucose unit and (average) M = 200 of an oxidized unit, accounting for the low degree of oxidation.*

The oxidation of maltodextrins was carried out with a less than stoichiometric amount of NaOCl and without heating the reaction mixture. The (expected) degree of oxidation is 60%. The procedure for the purification of the samples obtained in the experiments 1-3 was as follows: the reaction mixture was concentrated to about 20% of its original volume. After removal of the NaCl by dialysis the solution was freeze-dried.

b. *Oxidation of starch with the stoichiometric amount of hypochlorite*

The results of the experiments of series 2, in which experiments the stoichiometric amount of sodium hypochlorite (3 moles per mole glucose unit) was applied, are summarized in Table 2. Fig. 1. represents an example of a titration curve.

The oxidation in these experiments proceeded more quantitatively due to the higher amount of NaOCl and the heating of the reaction mixture after about 60% conversion. In most of the experiments of the second series the stoichiometric amount of hypochlorite was used i.e. the molar ratio hypochlorite/glucose unit is 3:1. The objective was to oxidize starch as completely as possible and to investigate the influence of the reaction parameters on yield and sequestering capacity of the respective products obtained. Important in this respect are the initial temperature, the pH and the aggregation state of the starch. The catalytic amount of bromide was varied from 3-6% (w/w starch). In two experiments a higher concentration was used. The initial concentration was approximately 0.02-0.08 M.

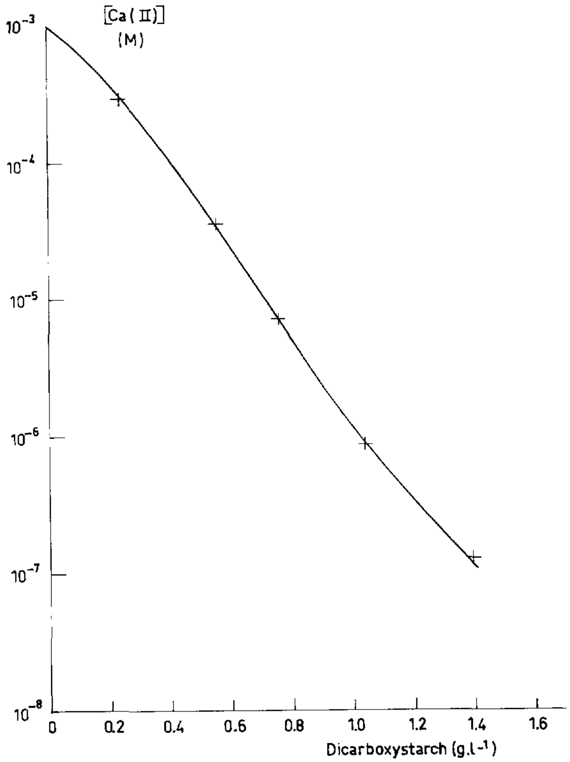

Fig. 1. Example of a titration curve of dicarboxy-starch (prepared at 5 °C, C_{Br^-} = 0.04 M cf. Table 2, exp.13). Free Ca(II) was measured with an ion selective electrode.

Table 2. The bromide-catalyzed oxidation of linear dextrins and wheat starch with NaOCl.

Exp.[1]	sub-strate	pH	NaOCl (% of theoretical amount)	bromide (%)[2]	T[3] (°C)	Y[4] (%)	SC (mmole Ca/g)	CC[4] (%)
1	S(g)	7-10	80	5	20	65	0.90	65
2	S(s)	7-10	80	3	20	80	1.10	80
3	LD	9-10	80	10	20	60	0.75	69
4	S(s)	9.0	100	6	20	95	0.70	64
5	S(s)	9.0	100	6	5	95	1.33	62
6	S(s)	9.5	100	6	20	98	1.11	71
7	S(s)	9.5	100	3	20	84	1.20	69
8	S(s)	9.5	100	12	20	69	1.25	62
9	S(s)	9.5	100	6	5	98	1.37	75
10	S(s)	9.5	100	3	20	95	1.15	71
11	S(s)	10.0	100	6	20	86	1.38	76
12	S(s)	10.0	100	3	20	86	1.20	70
13	S(s)	10.0	100	6	5	97	1.38	76

[1] *Abbreviations: S = starch, s = solid form, g = gelatinized starch, LD = linear (amylo)dextrins. SC = sequestering capacity. CC = carboxylate content with respect to the theoretical amount at 100% conversion (8.47 mmole COONa/g).*

[2] *w/w starch (initial bromide concentration is approximately 0.02-0.08 M).*

[3] *Initial temperature.*

[4] *Yield (Y) was calculated on basis of M = 162 of an anhydroglucose unit and M = 236 of an oxidized unit (as disodium salt). The calculation of the carboxylate content was based on M = 192 of the free acid.*

c. *Large-scale preparations of dicarboxy-starch*

The results of the large-scale preparations of dicarboxy-starch and of an electrochemical oxidation of starch are presented in Table 3.

Table 3. Large-scale oxidation of wheat starch at pH 9.5 and low temperature.

Experiment[1]	T (°C)	bromide(%, w/w on starch)	yield (%)	SC (mmole Ca/g)
1	0-15	5	95	1.2
2	0-5	5	95	1.4
3	0-10	5	95	1.3
4	2-4	5	91	1.3
5	17	25	80	1.0

[1] *Experiment 1-3: 100 - 150 g scale; experiment 4: 5 kg scale; in experiments 1-4 the pH was kept at 9.5. Experiment 5 concerns an electrochemical preparation carried out on a 200 g scale and at pH 9.8-10.2.*

The results of these experiments are in agreement with those reported in Table 2, both with respect to yield and sequestering capacity of the products. However, the material obtained via the electrochemical production has a lower SC. Apparently this production method needs further optimization.

Discussion

Yield and sequestering capacity

The most important aspects of the bromide-catalyzed hypochlorite oxidation to be considered are the yield and the sequestering capacity of the products in relation to the reaction conditions.

The yield varied somewhat: 85-95%, but the small differences are in our opinion mainly attributable to (inevitable) small differences in the work-up procedure; also the oxidation degree will influence the yield to a slight extent.

Comparison of the results given in Table 1 and Table 2 clearly shows that the oxidation degree is an important factor with respect to the sequestering capacity of the product. The sequestering capacity of the dextrins, which were converted with 60% of the theoretical amount of oxidant is about 0.5-0.6 mmole Ca/g, whereas that of the com-

pletely oxidized dextrins is about 0.75 mmole Ca/g. The sequestering capacity of the 60% oxidized material also appears to be lower than that of the completely oxidized starch.

In Table 2 it is seen that the sequestering capacity, which generally lies between 0.7 mmole and 1.4 mmole Ca/g, appears to be influenced by all reaction parameters i.e. pH, temperature and catalyst concentration. The experiment at pH 9.0 and at 20 °C yields a product with a sequestering capacity of 0.70 mmole Ca/g (exp. 4); oxidation under similar conditions but at a lower initial temperature (0 - 5 °C) yields a product with a higher calcium sequestering capacity (1.33 mmole Ca/g, exp. 5). At pH 9.5 a similar effect is observed: the sequestering capacity of the product prepared at 5 °C is 1.37 mmole Ca/g (exp. 9), whereas the sequestering capacity of the material prepared at 20 °C amounts to 1.11 mmole Ca/g (exp. 6).
It is remarkable that at pH 10 the temperature seems to be no longer of importance with respect to the sequestering capacity: both products, obtained with 6 % (wt) catalyst have a sequestering capacity of about 1.4 mmole Ca/g; however, the yield of the former experiment seems to be somewhat lower.
It can be concluded that an initial low reaction temperature is favourable for the preparation of products with a high sequestering capacity; when the pH increases from 9 to 10 the influence of applying a lower temperature diminishes.
Another effect is seen in the catalyst concentration. The higher the concentration of bromide, the higher the sequestering capacity of the products (*cf.* experiments 6-8, 9-10 and 11-12 in Table 2).

It is also interesting to compare the results of this study and those from *Floor* et al. [31]. These authors have extensively investigated the hypochlorite oxidation and characterized the products, obtained via this procedure and those, prepared by consecutive oxidation with sodium periodate/sodium chlorite. Especially the factors, which influence the sequestering capacity of the oxidized starches were the subject of their study. The sequestering capacity of the products, obtained via the two step procedure ranges between 2.0 and 2.5 mmole Ca/g. The products prepared from starch have retained their high molecular weight (DP >1000). The NaOCl-oxidation resulted in compounds with a much lower sequestering capacity (about 1 mmole Ca/g); it was also observed that substantial degradation had taken place. *Floor* et al. [31, 32, 34] concluded that the molecular weight of the product is the most important factor in determining the sequestering capacity of dicarboxy-starch. However, it can be derived from their experiments that the sequestering capacity depends strongly on the oxidation degree too. It was established that repeated hypochlorite oxidation of an isolated product resulted in a material with a higher carboxylate content (an increase of 25%) and despite its much lower molecular weight, a much higher sequestering capacity (1.77 mmole Ca/g, being an increase of 65%). In chapter 6 of this thesis this subject will be discussed in more detail.

Both the behaviour of the various oxidizing species, HOBr, HOCl, OBr^- and OCl^-, and the oxidation sequence of the starch will influence the carboxylate content and herewith the yield and the sequestering capacity of the products.

Side reactions of the oxidant

So far the mechanism of the hypochlorite and the hypobromite catalyzed oxidation has not been elucidated. There is evidence that the reactive species is an intermediate, formed from hypochlorous acid and its anion [42, 55], because the maximum rate of the hypochlorite oxidation is found in the region at pH 7 and neither HOCl nor OCl^- have its maximum at this pH. The reactivity of $HOCl/OCl^-$ may result from the formation of Cl- or O-atoms or ClO- and OH-radicals. Whether an analogous mechanism occurs in the hypobromite oxidation is still unknown. This topic will be discussed in chapter 4 and 5 of this thesis. It is evident that the presence of HOCl and OCl^- beside HOBr and OBr^- will make the system more complicated.

The most important (undesired) reaction of these oxidants concerns the irreversible disproportionation according to :

$$3\,HOCl \rightarrow 2\,HCl + HClO_3 \quad (1)$$

$$3\,HOBr \rightarrow 2\,HBr + HBrO_3 \quad (2)$$

and mixed reactions.

In most of the experiments described above we have used stoichiometric amounts of hypochlorite. The consequence of any formation of (non-reactive) chlorate and/or bromate, is that under these conditions starch is not completely oxidized and the product obtained has a lower carboxylate content and a lower sequestering capacity.
The rate of the reaction of the self-decomposition of HOCl is the highest at pH 7 [36, 53]; the highest rate for the disproportionation of HOBr is found at approximately pH 9 [48], but the rate decreases considerably at higher and lower pH. Also higher temperatures enhance the formation of chlorate or bromate. The results of our experiments indicate that incompletely oxidized products may arise at unfavourable conditions, as is reflected by the results listed in Table 2. Especially at pH 9 and 20 °C such compounds seem to be formed. The sequestering capacity of the product oxidized at 5 °C differ to a large extent from the product prepared at 20 °C. The optimum yield and performance are found when starch is oxidized at pH 10 and at 0-5 °C. Apparently the oxidant is sufficiently stabilized at this pH. It has to be stressed that also the behaviour of the intermediates in the starch oxidation may be responsible for these phenomena. This possibility will be discussed below.

Intermediates and mechanism

The formation of stable or low-reactive intermediates will result in products with a relatively small sequestering capacity.

Theoretically two intermediate products, 2-keto and 3-keto-starch, may arise after the first reaction step. Fig. 2 shows the 3-keto-form. Both intermediates as well as the 2,3-diketo-consecutive structure may form hemi-ketal compounds (see for an example Fig. 3).

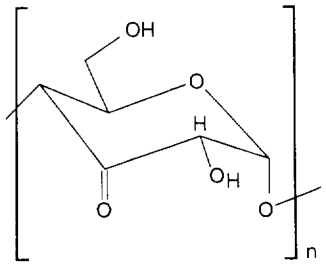

Fig. 2. An intermediate structure of a product after the first oxidation step of starch with sodium hypochlorite.

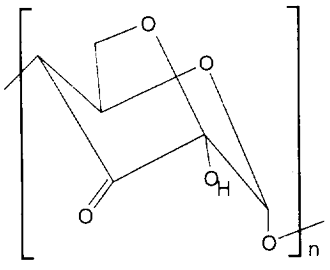

Fig. 3. Stable intermediate structure in the oxidation of starch with sodium hypochlorite, formed by intramolecular acetalization of the 2,3-diketo-form.

Evidence for the formation of relatively stable intermediates has been presented earlier by *Prey* and *Fischer* [56, 57]. These authors have shown that upon oxidation of starch with hypochlorous acid at pH between 7 and 8 mainly products with carbonyl groups are formed, whereas at higher pH (9-10) mainly carboxylate groups are introduced. The fact that the products prepared at pH 10 following our procedure have a higher sequestering capacity than those prepared at lower pH suggests that these carbonyl compounds may react in two ways, either a ketal compound is formed or reaction with $HOBr/OBr^-$ occurs. When the oxidation of the intermediate shown in Fig. 3 is (too) slow, hemi-ketal compounds may arise, which eventually will be oxidized yielding lactones (*cf* Fig. 4.)

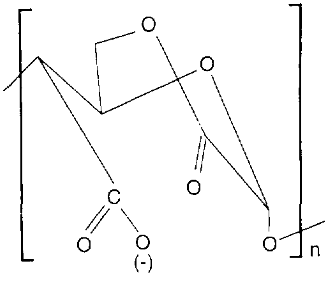

Fig. 4. Intermediate carboxy (lactone) in the oxidation of starch.

This reaction sequence has the following consequences:

- the stoichiometric amount of sodium hypochlorite is consumed
- the amount of carboxylate groups is lower than expected
- especially at lower pH the formation of ketal compounds seems to be enhanced, and the products formed at these conditions will have a lower SC.

Another indication for the occurrence of side reactions is given by the fact that the product in the acid form shows an anomalous behaviour upon titration. The product is converted into the acid by ion exchange and isolated by freeze drying of the solution. The carboxylate content is determined by titration with 0.2 N NaOH.
It is however observed that after the neutralisation point (pH 10) is reached, a slow though immediate decline of pH starts. This effect is more pronounced at higher temperature, probably due to the higher reaction rate. About 15% additional NaOH-solution is required to maintain the pH at 10. This behaviour may be attributed to the presence of lactones, which are subject to slow hydrolysis under these conditions to yield dicarboxylate starch.

It is clear that two phenomena may be responsible for the fact that the products prepared at low pH have a lower performance:

- disproportionation of the reagent
- formation of stable or low reactive intermediates.

Conclusions

The use of sodium bromide as a catalyst in the hypochlorite oxidation of starch offers several advantages:

- a higher calcium sequestering capacity is obtained

- white products are obtained
- despite the fact that a low hypochlorite concentration is maintained the reaction can be finished within one day, which gives perspectives for the production of dicarboxy-starch via an electrochemical process as well as for large-scale preparation.

The pH optimum is found at 10 which is higher than that of the non-catalyzed reaction. The better performance of the products may be ascribed to the fact that at high pH the decomposition of the oxidant is prevented, leading to a higher degree of oxidation. Moreover, at low pH the formation of lactones is enhanced, which may exhibit a low reactivity for further conversion.

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CHAPTER 3

THE HYPOCHLORITE OXIDATION OF INULIN

Summary

The oxidation of inulin with hypochlorite in the presence of sodium bromide as the catalyst has been investigated. The main objective of this study was to establish the calcium binding properties of the product, 3,4-dicarboxy-inulin, and to optimize the reaction conditions for the preparation.

It was found that the products are obtained in high yields (80-95%) and exhibit good to excellent calcium sequestering properties. Typical values for the sequestering capacity (SC) of the products are 2.0-2.3 mmole Ca/g dicarboxy-inulin, prepared from chicory-inulin (average DP = 10). Dahlia inulin (average DP = 30) yields an even somewhat better performing product (2.5 mmole Ca/g). Hence they are potential candidates for replacement of the substances nowadays used as co-builders in laundry detergent formulations e.g. sodium tripolyphosphate, zeolite and polycarboxylate. The most suitable conditions for the preparation with bromide as a catalyst are found at pH 10. Without catalyst good results are obtained when the stoichiometric amount of NaOCl is added at once to the inulin solution and the pH is kept at 9.

Introduction

The specific glycolic oxidation of various polysaccharides yields dicarboxylate compounds which possess good calcium binding properties [1-3] and consequently can replace the synthetic polycarboxylates which are now in use as co-builder [4] in laundry detergents [5, 6]. Because of the non-biodegradability of synthetic polycarboxylates a substitute is desirable. It is expected that oxidized carbohydrates will be better in this respect.
Carbohydrates which have been investigated extensively as polycarboxylate-precursor are starch and its components amylose and amylopectin [7-11], dextrins [7-9], cellulose and hemicellulose-containing substances [3, 4]. Starch-derived polycarboxylates appear to be the most promising. However, there is some doubt about the biodegradability of the high molecular weight materials [3]. Because the Ca-binding of dicarboxy-starch with a lower molecular weight is less strong and possibly falls short for application as co-builder in laundry detergents, there is a need for a polycarboxylate with a relatively low molecular weight[1] and with a good calcium-binding performance.

The calcium binding properties of oxidized glucans are attributed to the multiple occurrence of the oxydiacetic acid (ODA) moiety (*cf.* Figure 1).
This structural feature is very suitable for the binding of calcium [10, 12]. With calcium ions a W-shaped structure is formed in which the carboxylate groups and the ether oxygen atom are involved. Upon oxidation of starch this structural feature is obtained only frequently after a high degree of oxidation because the oxidation of two adjacent glucose units is required (see chapter 6 and 7).

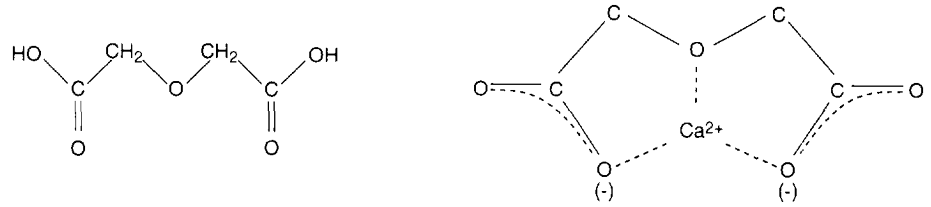

Fig. 1. Structure of oxydiacetic acid (ODA) and its calcium complex.

A polysaccharide in which the ODA-structure is obtained directly upon glycolic oxidation is inulin, *cf.* Figure 2.

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[1] It is expected that oxidized products with a low molecular weight are better biodegradable [3].

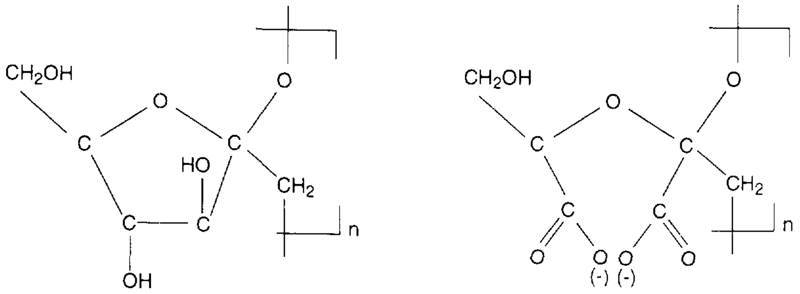

Fig. 2. Structure of inulin and the ODA-structure in oxidized inulin.

It is therefore to be expected that oxidized inulin will be a good calcium binding agent. So far this hypothesis could not be confirmed, due to the lack of a suitable preparation method.

Two methods are available for the oxidation of the vicinal diols in carbohydrates:

1. a two step oxidation procedure with sodium periodate and sodium chlorite/hydrogen peroxide. Both steps are carried out in acidic medium.
2. a one-step oxidation with sodium hypochlorite. This oxidation is carried out in alkaline solution.

In the oxidation of starch and cellulose the former procedure yields better performing products. However, *Nieuwenhuizen* et al. [6] found that the products which were prepared from inulin had only a poor calcium binding capacity. *Floor* et al. [13], using an improved method for the second step of this procedure, obtained similar results.

A possible explanation for these disappointing results is the formation of relatively stable hemi-acetal compounds in the first oxidation step. From starch it is known that in the so-called dialdehyde starch practically no free aldehyde groups are found: the material mainly contains inter and intra hemi-acetal groups. An example of such a (hypothetical) structure resulting upon inulin oxidation is given in Fig. 3. In the second step hydrolysis of these groups is necessary before oxidation may occur. When this hydrolysis step is slow the oxidation with sodium chlorite will be retarded and exceptionally long reaction times will be required. Neither *Nieuwenhuizen* et al. [4] nor *Floor* et al. have investigated this aspect. In order to avoid the formation of acetal or ketal compounds the oxidation has to be carried out in neutral or alkaline medium.

Therefore the second procedure, oxidation with NaOCl, may be more suitable for this purpose, because the reaction is carried out at pH 8-9. However, it has been shown that oxidation of starch with NaOCl yields products with a lower calcium sequestering capacity.

In a previous study [14] we have indicated some reasons for this and we have also shown that improvements are possible. Thus the use of sodium bromide as a catalyst in the reaction improves both the reaction rate and the quality of the products. Moreover, the reaction can be carried out at higher pH (9-10.5) so that hemi-acetal formation of intermediates will be prevented.

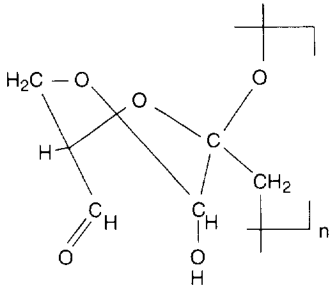

Fig. 3. Hemi-acetal structure of dialdehyde inulin.

After a few exploratory experiments it was established that inulin upon oxidation with sodium hypochlorite in the presence of bromide indeed yields products which have better calcium binding properties than those prepared from starch [15]. Also evidence was obtained that the products from inulin prepared in this way are much better calcium sequestering agents than dicarboxy-inulin as obtained by *Nieuwenhuizen* et al. [4]. In this paper we present details about our investigations on the influence of the respective variables involved in the oxidation of inulin with as main objective to optimize the process for the preparation of dicarboxy-inulin. The variables studied include:

- mode of the addition of the oxidant
- temperature
- pH
- reaction time

in relation to the yield and the properties of the product, specifically the calcium sequestering capacity and the number of carboxylate groups introduced.

Experimental

Materials

In the respective series of experiments two types of inulin were studied:

1a. inulin, isolated from chicory root, was a gift from Suiker Unie (Roosendaal, the Netherlands); average degree of polymerization (DP) = 10

1b. inulin, isolated from chicory root, was obtained from Sigma chemicals; average DP = 10
2. inulin, with an average DP = 30 isolated from dahlia tubers, was obtained from Sigma chemicals.

The DP of these samples was determined by NMR spectroscopy, using the characteristic signals of the protons of glucose and fructose.
Sodium hypochlorite solutions were of commercial quality and prepared by passing chlorine gas into an aqueous solution of sodium hydroxide. The solution contained about 100 g/l Cl_2 and was stabilized with a slight amount of NaOH (0.3%).
Sodium hydroxide solutions were prepared from NaOH (p.a. quality Merck). Methanol and NaBr were obtained from Merck (p.a. quality); ethanol (96%) was obtained from Gist-brocades.

Methods

a. Oxidation

The oxidation of inulin was carried out in a 150 ml double-wall vessel, equipped with inlets for NaOH dosage and addition of sodium hypochlorite solution, and a combined pH glass electrode. The reaction mixture was stirred magnetically.
Three sets of conditions were applied (see Table 1-4). In the experiments of series 1 and 2 4.85 g (30 mM) of Sigma inulin was dissolved in 25 ml of water of about 50 °C and the solution was transferred to the reaction vessel. After cooling to 25 °C a known amount of sodium bromide was added, followed by a small amount of NaOCl-solution. After an initial sharp rise of the pH (11-11.5) a fast decline was observed which has to be attributed to acid formation. The stoichiometric amount of NaOCl or some excess (ca. 5-10%) was added in the course of 6-8 hrs (unless otherwise indicated). The objective was to maintain a low concentration of NaOCl/NaOBr in order to prevent the decomposition of the oxidant. Throughout the experiment the pH was kept constant by addition of NaOH-solution, which was controlled by a pH stat. After addition of the reagent was complete the temperature was raised gradually to about 45 °C (in the experiments of series 2). The reaction time was generally 20-24 hours.

In the series 3 4.85 g (30mM) of inulin (Suiker Unie) and 270 mg of NaBr were dissolved in water (25 ml) and after cooling to 25 °C 80 ml of sodium hypochlorite solution (90mM) was added at once. The pH was adjusted to the desired value by slow and careful addition of a small volume of 50% aqueous acetic acid solution to the well-stirred reaction mixture.

After consumption of about 60% of the oxidant (usually after about 6 hours) the temperature was gradually raised to 45-50 °C. The reaction time was generally about 24 hours after which >95% of the sodium hypochlorite was consumed.

The experiments of series 4 were carried out in the same way as those of series 3, but instead of 80 ml 100 ml NaOCl-solution with a somewhat higher concentration was used (resulting in about 30% excess of oxidant). In these experiments also Suiker Unie inulin was used.

For the isolation of the dicarboxy-inulin (as disodium salt) the procedure was as follows: the reaction mixture was concentrated in vacuo to a volume of about 50 ml. The solution was poured into 150 ml well-stirred 96% ethanol. After standing for one day the liquid was decanted from the oily residue.[1] The residue was dissolved in 50 ml demineralized-water and poured into 175 ml absolute methanol.
In order to avoid oil formation this procedure was carried out very carefully i.e. small amounts of the solution were added slowly to the well-stirred methanol. A white solid was obtained, which was collected by filtration and dried in vacuo at 50 °C. This material usually is contaminated with small amounts of inorganic salts, water and methanol. The percentage of dicarboxy-inulin and the carboxylate content were determined by converting the material into the acid form (see below).
The calculations of percentage dicarboxy-inulin and yield were based on M = 236 for the disodium salt of dicarboxy-inulin, M = 192 for the acid form and M = 162 for the substrate.

b. Determination of the sequestering capacity

The calcium sequestering capacity (SC) was determined by measurements of the Ca(II) concentration with an ion selective electrode. The procedure was as follows. To 100 ml of an aqueous solution containing 10^{-3} M Ca(II) and 5.10^{-3} M NaCl, known amounts of dicarboxy-inulin (disodium salt) were added. If necessary the pH was adjusted between 10-10.3. After 2 minutes of stirring the resulting concentration Ca(II) was measured. From the titration curve (see Fig. 4) the amount needed for lowering the concentration to 10^{-5} M Ca(II) was found by interpolation. For the calibration of the Ca(II) selective electrode aqueous solutions of 10^{-2}, 10^{-3}, 10^{-4}, 10^{-5} and 10^{-6} M $CaCl_2$ and 5.10^{-3} M NaCl were used. The calibration curve (log U vs. concentration Ca(II) was linear between 10^{-2} and 10^{-5} M; below the latter

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[1] In most cases an oil is formed; if a solid is obtained the material is collected by filtration. When in the second precipitation step an oil is formed, it is converted into solid material by addition of absolute methanol to the oily residue. After stirring for a few hours the material has solidified and can be collected by filtration.

concentration the sensitivity of the electrode decreases in accordance with the specifications of the supplier. However, again a linear relationship is observed and reproducible measurements could be carried out to C = 10^{-8} M Ca(II).
The calcium sequestering capacity is defined as the number of mmole Ca(II), that will be bound by one gram of sequestering agent at the conditions given above until the concentration of non-bound Ca(II) is 10^{-5} M. This value is considered to be the upper limit in the washing process at which practically no incrustation occurs.
Another approach of characterizing the material with respect to calcium binding is measuring the intrinsic complex constant (K_{int}). *Floor* [11] has shown that for oxidized polysaccharides the method of *Tanford* [16] has to be applied. Because inulin is a relatively small polymer the approach which has been used by *Floor* may be less meaningful for the present material. However, to allow a comparison with dicarboxy-starch, we shall give some results (see Table 5).

c. Determination of the carboxylic acid content and of the yield

A known amount of the substance was converted into the acid form by ion exchange (Amberlite IR120, H^+form). The solution was subsequently freeze-dried, herewith removing water, methanol, HCl and HBr. From the weight observed the percentage of dicarboxy-inulin was calculated. The samples were dissolved in water and titrated with 0.2 M sodium hydroxide solution to determine the carboxylic acid content.

Results

The results of the first series of experiments, concerning the (incomplete) oxidation of inulin, are summarized in Table 1. The aim was to establish the adequate conditions for for the oxidation of inulin and to prove that this material yields a better calcium binding agent than starch. It appears that even at a relatively low degree of oxidation the material exhibits good calcium binding properties. However, it can be seen that, to obtain a high sequestering capacity, reaction times of about one day are needed. Furthermore, it was found that the sequestering capacity can be predicted by measuring the sequestering capacity of the reaction mixture.

The aim of the experiments carried out in series 2 was to establish the influence of the pH on the properties and the yield of the product. The results are presented in Table 2. The high calcium sequestering capacity of the oxidized inulin is to be noted. An example of a titration curve (sample from experiment 3, Table 2) is given in Fig. 4.

The structure of dicarboxy-inulin could be confirmed by ^{13}C NMR spectroscopy [4] see Fig. 5. From quantitative ^{13}C NMR measurements using a known amount of t-butanol

as internal standard the amount of dicarboxylate was found to be 65 ± 7%. This value is somewhat lower than follows from the chemical analysis.
Based on an Attached Proton Spectrum the signals are assigned as follows:
δ 180 -175.7 ppm COOH groups, δ 104 -105.3 ppm C_5, δ 71 -83 ppm C_2, δ 64 -66 ppm $C_1 + C_6$.

Table 1. Partial oxidation of (Sigma chicory) inulin with sodium hypochlorite [1] and NaBr as the catalyst.

Exp.	pH	C_{Br^-}[2] (M)	SC(i)[3] (mmole Ca/g)	SC(s)[4] (mmole Ca/g)	Remarks
1	8.7-9.3	0.1	0.60	nd	2 hrs reaction time; 40% NaOCl consumed
2	8.7-9.3	0.2	0.60	nd	3 hrs reaction time
3	8.7-9.3	0.2	0.85	1.1	
4	9.0	0.2	1.1	1.4	
5	9.0	0.1	nd	1.7	24 hours reaction time
6	9.5	0.1	nd	1.6	

[1] *In all experiments the stoichiometric amount (3 moles/fructose unit) of the reagent was gradually added (cf. paragraph Experimental).*

[2] *Initial concentration of bromide; the final concentration was about 25% of this value.*

[3] *SC(i) = Estimated sequestering capacity of the material in solution; a 90% yield is assumed.*

[4] *SC(s) = Sequestering capacity of the solid material.*
nd = not determined.

A survey of the results of the third series of experiments is given in Table 3. In these experiments the reagent was added *at once*.

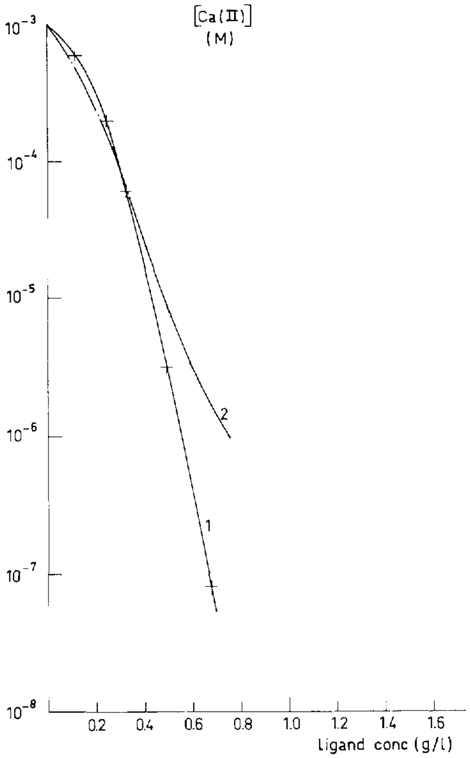


Fig. 4. Calcium ion concentration in water (10^{-3} M) as a function of the dicarboxy-inulin concentration (1: SC(s); 2: SC(i)).

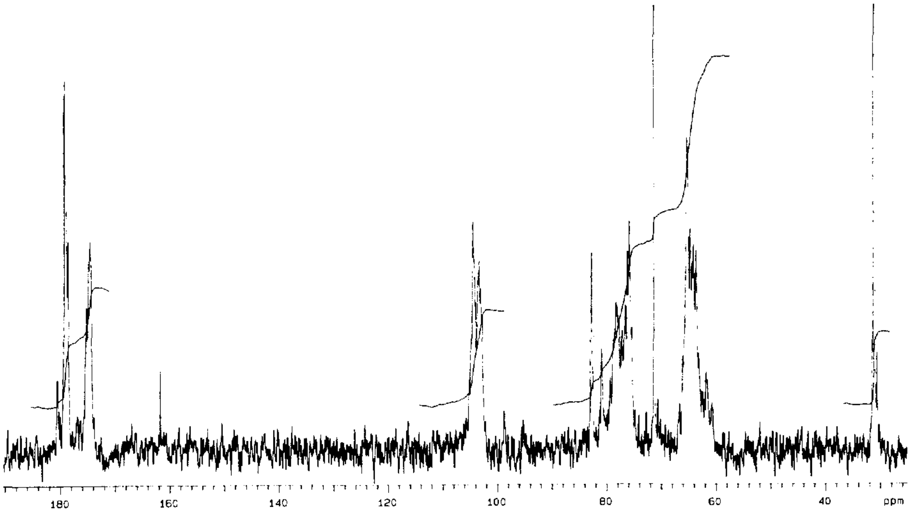


Fig. 5. ^{13}C NMR spectrum of dicarboxy-inulin.

Table 2. Oxidation of inulin (chicory, Sigma) with sodium hypochlorite and sodium bromide as the catalyst with gradual addition of the reagent.

Exp.[1]	pH	$C_{bromide}$ [2] (M)	NaOH added (mmole)	SC(i)[3] (mmole Ca/g)	SC(s)[4] (mmole Ca/g)	Y[5] (%)	CC[5] (%)
1	8.5	0.03	63	1.9	2.1	98	73
2	9.0	0	65	2.2	2.4	82	75
3	9.0	0	62	2.2	2.2	87	68
4	9.0	0.03	60	nd	2.0	83	67
5	9.0	0.03	70	1.9	2.0	88	69
6	9.0	0.03	70	1.9	1.9	85	70
7	9.5	0.03	74	1.8	2.0	92	83
8	9.5	0.06	71	1.8	2.0	95	60
9	9.5	0.06	71	1.8	2.0	89	86
10	10.0	0.06	75	1.7	2.1	86	78

[1] *In experiments 2 and 3 the stoichiometric amount of NaOCl (3 moles of NaOCl per mole of anhydrofructose unit) was added at once. In the other experiments this amount was added in the course of 6-8 hours. In all experiments 4.85 g of chicory inulin (Sigma) was used.*

[2] *Initial concentration of bromide; the final concentration is about 25% of this value.*

[3] *SC(i) = estimated sequestering capacity of the material, determined by measuring SC of the solution; a 90% yield is assumed.*

[4] *SC(s) = Sequestering capacity of the solid material.*

[5] *Yield (Y) and Carboxylate content (CC) were calculated with M = 162 for an anhydrofructose unit, M = 192 for an oxidized unit in the acid form, and M = 236 for an oxidized unit as disodium salt.*

nd = not determined.

Table 3. Oxidation of inulin (chicory, Suiker Unie) with sodium hypochlorite and sodium bromide as the catalyst with addition of the reagent at once.

Exp.[1]	pH	NaOH (mmole added)	SC(i)[2] (mmole Ca/g)	SC(s)[3] (mmole Ca/g)	Y[4] (%)	CC[4] (%)
1	8.5	47	1.5	2.0	50	83
2	8.5	50	1.55	2.1	nd	nd
3	9.0	56	1.55	1.8	72	66
4	9.5	56	1.7	1.9	84	77
5	9.5	57	1.7	2.0	52	82
6	9.5	58	nd	2.1	72	92
7	10.0	64	2.1	nd	nd	nd
8	10.0	65	2.3	2.4	73	83
9	10.0	65	2.1	nd	nd	nd
10	10.0	66	2.2	2.3	85	81
11[5]	9.5	65	2.4	2.5	72	92

[1] *4.85 g of (chicory) inulin, the stoichiometric amount of NaOCl and 270 mg of NaBr were used. The NaBr concentration (0.025 M was practically constant throughout the experiment.*

[2] *SC(i) = estimated sequestering capacity of the material, determined by measuring SC in solution; a 90% yield is assumed.*

[3] *SC(s) is the sequestering capacity of the material isolated (corrected for the presence of impurities).*

[4] *Yield and carboxylate content (see note 5 of Table 2).*

[5] *In exp. 11 dahlia-inulin was used.*

nd = not determined.

The results of the fourth series of experiments, carried out with the aim to investigate the effect of applying an excess of 30% of the oxidant on the calcium binding properties of the product, are presented in Table 4.

Table 4. Oxidation of inulin (chicory, Suiker Unie) with 30% excess of sodium hypochlorite.

Exp.[1]	pH	NaOCl(mM)	NaOH (mmole added)	SC(s)[2] (mmole Ca/g)	Y[3](%)	CC[3](%)
1	8.0	115	51	1.85	74	74
2	8.5	115	65	2.1	80	80
3	9.0	122	73	2.2	58	86
4	9.5	131	82	2.2	72	78
5	10.0	120	65	2.3	73	86
6	10.25	135	90	2.4	70	89
7	10.5	125	70	2.1	81	81
8	10.5	138	84	2.3	79	89

[1] *In these experiments 4.85 g of inulin and 270 mg of NaBr were used. The bromide concentration was practically constant throughout the experiment. The initial concentration of bromide was approximately 0.025 M. About 30% excess of sodium hypochlorite was used.*

[2] *SC(s) is the sequestering capacity of the isolated material (corrected for the presence of impurities).*

[3] *Yield and carboxylate content (see note 5 of Table 2).*

In Table 5 a survey of the sequestering capacity and log K_{int} of some representative samples is presented. It may be seen that at low calcium concentration the binding of dicarboxy-inulin appears to be very strong. In chapter 7 of this thesis this topic will be discussed in more detail.

Table 5. Intrinsic calcium complex constants of some representative samples.

Sample[1]	SC mmole Ca/g	log K_{int}
2-2	2.4	9.6
2-3	2.2	9.7
3-2	2.1	8.6
3-3	1.8	8.3
4-1	1.85	9.0
4-5	2.4	7.8

[1] *Sample number: first figure refers to table number, second figure to experiment number.*

Discussion

Structure

The structure of dicarboxy-inulin was confirmed by ^{13}C NMR spectroscopy (*cf.* Fig. 5). From ion exchange and determination of the carboxylic acid content evidence was obtained that the material may contain lactones. Thus it was observed that dicarboxy inulin (acid form) shows an anomalous behaviour upon titration. By ion exchange of the disodium salt the acid form is obtained. After neutralisation of the material by addition of NaOH-solution (at approximately pH 10) the pH declines gradually in the course of minutes and more NaOH is needed to keep the solution at pH 10. The amount of extra NaOH is 7-10%. Heating of the solution fastens the pH decline. This behaviour points to the presence of lactones. It cannot be excluded that they are formed during the ion exchange and isolation procedure. Additional evidence for a reaction sequence in which lactones are formed during the preparation of dicarboxy-inulin originates from some experiments, not reported in detail in this chapter. They were carried out according to the procedure described for the oxidation of inulin of series 3. After complete consumption of the hypochlorite no further consumption of NaOH occurred. After addition of NaOH to raise the pH from 10 to 11.5 and upon heating at 45-50 °C it appeared that the pH declined slowly. It was necessary to add more NaOH (about 8% extra) to keep the pH constant. The lactones seem to be relatively stable at pH 10 and hydrolyse only at higher pH and temperature. More investigations about this subject with respect to formation and structure seem to be desirable. The occurrence of such lactonic material might be explained by the reaction sequence, which will be discussed below.

Comparison of the properties of dicarboxy-inulin and dicarboxy-starch

In this study several aspects of the hypochlorite oxidation of inulin have been investigated e.g. pH, mode of addition of the reagent and role of the catalyst and the characterization of the products with respect to the calcium binding properties.

As has been mentioned above a prediction of the sequestering capacity can be made by determining the sequestering capacity of the reaction mixture. Generally the sequestering capacity which has been determined in the reaction mixture of these experiments, is slightly lower (about 5-10%) than that of the isolated product. It should be emphasized that the former is based on 90% yield and that small differences in yield will cause differences between SC(i) and SC(s). In some cases a significant difference is observed. An explanation for this discrepancy will be discussed below.

The most important conclusion is that under suitable conditions oxidized inulin binds calcium to a considerable extent. The SC of the best performing product is 2.3 - 2.5 mmole Ca/g. It is remarkable that the use of bromide is not required i.e. the best performing product is obtained when only sodium hypochlorite is used (*cf.* Table 2, experiment 2).

As expected the highest sequestering capacity was found for the fully oxidized compounds. In a previous study (chapter 2 of this thesis) we have shown that oxidized starch, prepared in an analogous procedure yields products with a lower SC, namely up to 1.4 mmole Ca/g. The SC of the inulin derived products is comparable to that of the high molecular weight and completely oxidized starches, which have been obtained via a two step procedure (2-2.5 mmole Ca/g) [7].

It is clear that oxidation of inulin yields a better calcium binding material than starch prepared by oxidation with the hypochlorite/sodium bromide system.

Effect of pH and of mode of addition of the oxidant on the performance of the products

Three methods have been investigated.

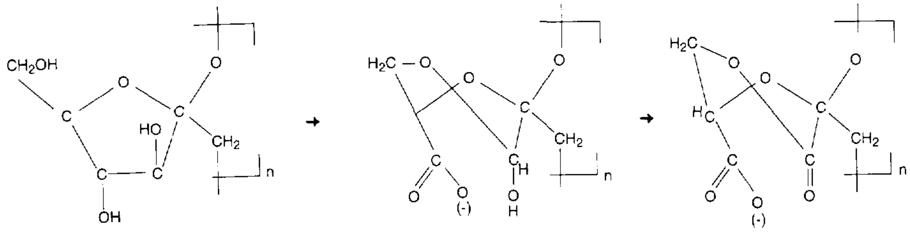
1. Gradual addition of sodium hypochlorite to a solution of inulin and bromide (see Table 2). According to this procedure the differences with respect to yield and performance of the products are small i.e. the yield varies from 82 to 98% and the SC from 1.9 to 2.1 mmole Ca/g. For comparison, the SC of sodium tripolyphosphate is 2.0 mmole Ca/g and of Sokalan, one of the major synthetic polycarboxylates, amounts to 2.75 mmole Ca/g.
2. Addition of the theoretical amount or excess of sodium hypochlorite *at once* (*cf.* Table 3). The optimum pH for the preparation of dicarboxy-inulin as follows from these experiments is somewhat higher than in the foregoing experiments namely 10. It appears that the products have a somewhat higher sequestering capacity than those obtained in series 2. The yield is somewhat lower (generally about 80%)
3. The effect of the use of an excess of oxidant on the quality of the product and yield.

(see Table 4). The yield seems to be somewhat less than in the corresponding experiments in which the theoretical amount of NaOCl was used. The excess of oxidant possibly leads to some destruction of the dicarboxy-inulin. Formation of tricarboxy-inulin cannot be excluded, but it seems improbable that this compound has less satisfying properties. Both the behaviour of the oxidant and the intermediate products may explain the differences as seen in sequestering capacity and yield.
Oxidation of inulin in the presence of a large amount of hypochlorite at low pH seems to be disadvantageous. The lower NaOH-consumption, despite the consumption of the theoretical amount of reagent after 24 hours reaction indicates that under these conditions disproportionation of the reagent occurs. As a consequence of this competitive reaction the substrate will be insufficiently oxidized.
At the conditions used in series 1 and 2 the hypochlorite/hypobromite concentration is much lower so that the formation of chlorate or bromate,

$$3\ NaOCl \rightarrow NaClO_3 + 2\ NaCl$$

$$3\ NaOBr \rightarrow NaBrO_3 + 2\ NaCl$$

being a second- or third-order reaction with respect to hypochlorite/hypobromite, is suppressed.
However, another reaction sequence, as depicted below, may influence the yield and properties of the products too.



The formation of hemi-ketals is expected to occur at lower pH. The consequence of the reaction sequence is that, in spite of the consumption of the same amount of oxidant, the NaOH-consumption is lower and the product will have a lower sequestering capacity. It is also to be expected that the material is less polar and that formation of lactones may explain the difference between SC(i) and SC(s). The lactone is possibly lost during the work-up, because this material is expected to be better soluble in methanol and ethanol than the disodium salt of dicarboxy-inulin. Since the sequestering capacity of the lactone will be lower than that of the dicarboxylate it means that material will be lost which has a low calcium binding capacity. Finally, loss of especially the lower molecular weight products with a low calcium sequestering capacity during work-up may occur.

Conclusions

Oxidation of inulin with the stoichiometric amount of sodium hypochlorite leads to the formation of dicarboxy-inulin in high yield (80-95%). These products possess a very good calcium sequestering capacity 2.0-2.5 mmole Ca/g, which is comparable with present-day commercial builders. Sodium bromide can be used as a catalyst to accelerate the oxidation, but contrary to the oxidation of starch, the quality of the products is not improved by the use of this catalyst.

The optimum conditions for the oxidation include high pH. This may be attributed to the fact that decomposition of the oxidant is prevented, so that the product will have a higher degree of oxidation.

Evidence is presented that a small part of the carboxylic groups is present as lactone, arisen from the oxidation of ketals, whose formation is enhanced at lower pH.

The products obtained from dahlia inulin are slightly better performing than the material obtained from the lower molecular weight chicory inulin.

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CHAPTER 4

THE KINETICS AND MECHANISM OF THE HYPOCHLORITE OXIDATION OF LINEAR DEXTRINS AND INULIN

Summary

The rate of the reaction of starch with sodium hypochlorite/hypochlorous acid is pH dependent. The maximum rate is found at pH 7 at which none of these species has its maximum concentration. It is therefore suspected that reactive species arise from a reaction in which both HOCl and OCl^- are involved and that this reaction is rate determining.
Support for this hypothesis follows from the fact that the oxidation rates of amylodextrins, a short chain linear amylose, and inulin in this system in the pH range 6.5-8.0 are equal.

Kinetic computer simulations in which the (hypothetical) rate determining reaction

$$2HOCl + OCl^- \rightarrow 2\,OH^{\cdot} + OCl^- + Cl_2$$

is included, gave over the pH range examined (6.5-9.0) and over the range of the oxidant concentration (0.07-0.75M) good agreement between calculated and experimental values. This overall agreement was not observed for models including the reaction of three mo-

lecules HOCl with one molecule of OCl⁻ or of the reaction of one molecule of HOCl and one molecule of OCl⁻, respectively

It is concluded that a radical mechanism gives a plausible explanation for the pH dependency of the reaction and the phenomena observed. The nature of the active species remains still unknown.

Introduction

Sodium hypochlorite is a widely applied reagent in the cellulose and starch industry [1, 2]. It is used for bleaching of cotton and preparation of thin-boiling starches. Upon oxidation of starch or cellulose with stoichiometric amounts of this reagent 2,3-dicarboxy-starch and 2,3-dicarboxy-cellulose are obtained, respectively [3-12].

Because of their calcium sequestering properties, these materials can be used as co-builder in detergent formulations as replacement of phosphate or of the nowadays widely used synthetic polycarboxylates [5-12]. Despite the importance and the interest in the hypochlorite oxidation the mechanism is poorly understood. Also the kinetics of this reaction has received only little attention. The most extended studies in this field concern the partial oxidation of cellulose [13-15]. In fact two species may be responsible for the reaction: HOCl and OCl⁻. In view of the fact that dissociation of hypochlorous acid starts at pH > 6 and is practically complete at pH > 9 it is remarkable that the optimum rate of the oxidation is found at pH 7, *cf.* Fig. 1.

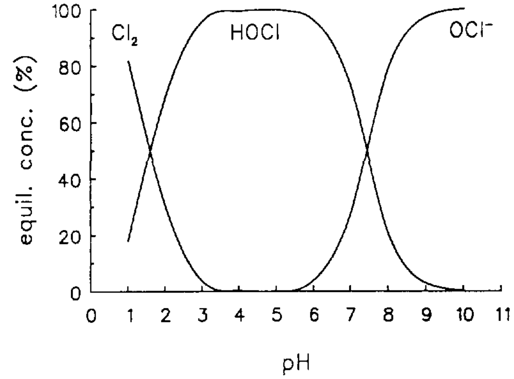


Fig. 1. The relative distribution of chlorine, hypochlorous acid and hypochlorite in aqueous solution as a function of pH at 20 °C [16].

If HOCl would be the reactive species the maximum rate is expected at pH < 5.5, whereas if OCl⁻, being the main species at pH > 9, would be the essential reactive entity the maximum rate is expected above this value. Because the optimum rate in the cellulose-oxidation is found at approximately pH 7 [13, 14], or slightly above 7 [4] in the reactive species, but that reactive species, arising from a reaction of HOCl and OCl^-, are responsible for the first step, as already postulated by *Epstein* and *Lewin* [13] and by *Nevell* and *Singh* [14, 15]. The anomalous behaviour in this reaction with respect to pH follows also from measurements by *Patel* et al. [17, 18] and *Schmorak* et al. [19] who investigated the kinetics of the hypochlorite oxidation. Surprisingly these authors did not account for the dissociation of hypochlorous acid. The rate constants as presented by them are based upon the net reaction

$$\text{starch} + HOCl_{total} \rightarrow \text{product(s)} + HCl^{1}.$$

Especially the authors who investigated the oxidation of cellulose have postulated several mechanisms and reactive species which should explain the pH dependence [13-15]. Their investigations were directed to determination of the pH at which the highest rate was found. The considerations on which the conclusions of these studies are based (with respect to the mechanism), have some shortcomings.

1. Expressions for the reaction rate are derived from the consumption of hypochlorous acid/hypochlorite without taking into account that disproportionation of these substances may contribute to a significant extent to the rate.

   $$3\ NaOCl \rightarrow NaClO_3 + 2\ NaCl$$

2. The reactions of starch and probably of cellulose too, lead to the formation of products which appear to be very reactive towards hypochlorous acid and hypochlorite [20, 21] and hence will contribute to the consumption of hypochlorous acid, even in the initial stage. This aspect has also been neglected.

The rate constants as mentioned in the literature are therefore too high (by approximately a factor 3)[2]. Also the mathematical treatment of the rate expressions [13-15] may be erroneous.

The following reactions differing in the extent of HOCl-participation have been considered [13-15]:

$$HOCl + OCl^- \rightarrow 2\ \text{reactive species: pH optimum 7.48 (R)}$$

---

[1] In which $HOCl_{total}$ means the sum of free HOCl and OCl^-

[2] In this chapter we will nevertheless maintain the rate constants as have been calculated and mentioned in literature.

$2\ HOCl + OCl^- \rightarrow$ 2 reactive species: pH optimum 7.22 (S)

$3\ HOCl + OCl^- \rightarrow$ 2 reactive species: pH optimum 7.00 (Q).

If one of these reactions should be rate determining, it can be shown that the differences between the respective reaction rates will be relatively small, as appears from Fig. 2.

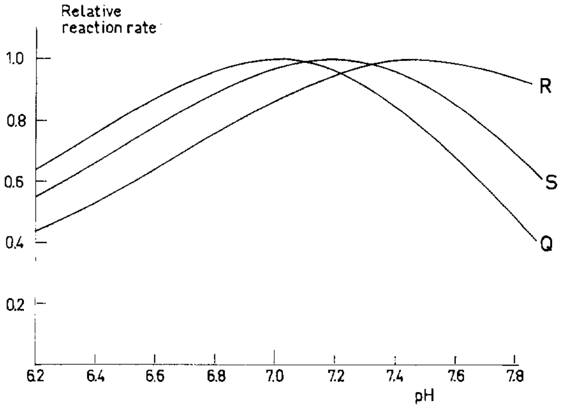


Fig. 2. The (relative) reaction rate of the hypochlorite oxidation as a function of pH for three mechanisms.

Because of these uncertainties we have carried out an experimental programme with the objective to measure the reaction rate at different conditions i.e. effects of pH, temperature, hypochlorite/hypochlorous acid and substrate concentration were investigated. Moreover amylodextrins, short chain amylose with average degree of polymerization (DP) = 25, and inulin (average DP = 10) were used as substrate. Because of the occurrence of consecutive and side reactions an analytical mathematical treatment was not expected to be meaningful. Instead we have tried to describe the processes by numerical simulation. In this chapter the results of this study are reported.

Experimental

Materials

Linear dextrins (amylodextrins) were prepared from waxy maize starch by enzymatic hydrolysis [22]. Gelatinized starch was incubated at 55 °C during 24 hours with a pullulanase (Promozyme, NOVO). The dextrins, which precipitated upon cooling, were collected by filtration, washed several times with methanol and dried in vacuo. The average degree of polymerization (DP) was 25 (determined by measuring the reducing capacity, according to the method of Nelson-Somogyi [23] and the total carbohydrate content according to the method of Dubois [24]). From HPLC-GPC analysis it appeared that the dextrins have a bimodal distribution [25].

Inulin, isolated from chicory roots was obtained from Sigma; the average DP was 10. The model compounds *trans*-1,2-cyclohexanediol, 1,3-cyclohexanediol (*cis/trans* mixture), 1,4-cyclohexanediol (*cis/trans* mixture) and 1,2-cyclohexanedione were obtained from Aldrich Chemie.

Sodium hypochlorite was of a technical quality, prepared by passing chlorine into a solution of sodium hydroxide in demineralized water. It contained about 100 g chlorine/l; for stabilization of the reagent the solution contained a slight excess of NaOH (about 3 g/l).
Acetic acid and the reagents for the titration of the sodium hypochlorite content of the reaction mixture (0.1 N sodium thiosulfate solution and potassium iodide) were obtained from Merck.

Apparatus and methods

The experiments were carried out in a 150 ml double-wall vessel, provided with an inlet for NaOH-dosage and a combined pH glass electrode. The pH was kept constant at the desired value by adding 4 M NaOH, controlled by a pH-stat (Radiometer).
The hypochlorous acid/hypochlorite concentration was measured by titration with 0.1 N thiosulfate in KI/acetic acid solution.
In 90 or 95 ml of hot water 2.0 g of substrate was dissolved and the solution was transferred to the reaction vessel. After cooling to 25 °C 10 ml or 5 ml, respectively of NaOCl-solution was added *at once* to the well-stirred solution, making the final volume of the reaction mixture 100 ml. The substrate concentration was 0.115 M; the NaOCl-concentration was 0.07 M and 0.14 M, respectively. The temperature was kept at 25 °C. During approximately 90 minutes the NaOCl-concentration was measured at regular time intervals. In one experiment a higher concentration of substrate was used (50 g of inulin/l, 0.28 M; the NaOCl-concentration was 0.15 M).
The various series of experiments which have been carried out had the following objectives:

a. comparison of the reactivity of dextrins, inulin and some model compounds,
b. measurement of the reaction rate of inulin and dextrins as a function of pH, NaOCl and substrate concentration and temperature.

In order to extend the data base for the computer modelling study the results of *Floor* et al. [11] have been used. These authors oxidized starch with hypochlorite at high concentrations of both oxidant (0.75 M) and substrate (0.25 M) in the pH region 7-9. The reagent was added at once to a suspension of starch. The procedure and the conditions were essentially the same as in our experiments; however, the temperature was somewhat lower (20 °C).

Experimental and computer simulation results

Comparison of the reactivity of amylodextrins and inulin

In Fig. 3 the results of the oxidation of amylodextrins and inulin with hypochlorite at pH 7.0 are presented. The results of a similar experiment at pH 8.0 (both with low and high hypochlorite concentration) are given in Fig. 4. It appears that in the pH range examined (6.5-8.0) the rates of the consumption of hypochlorite in the oxidation of starch and of inulin respectively are essentially the same.

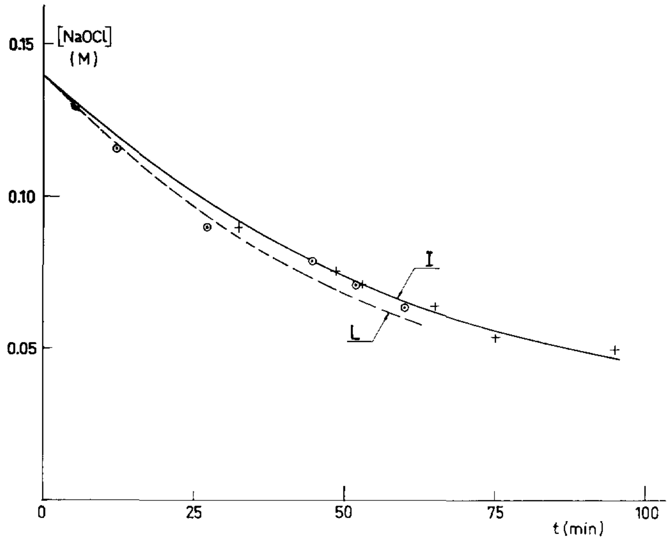


Fig. 3. Comparison of the reactivity of linear dextrins (L) and inulin (I) in the oxidation with hypochlorite (0.14 M) at pH 7.0 and 25 °C.

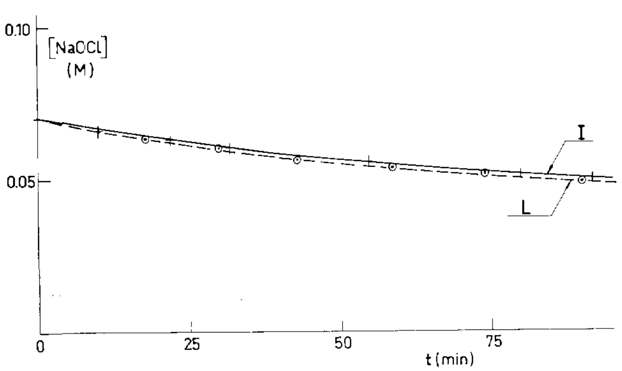


Fig. 4a. Comparison of the reactivity of linear dextrins (L) and inulin (I) in the oxidation with hypochlorite (0.07 M) at pH 8.0 and at 25 °C.

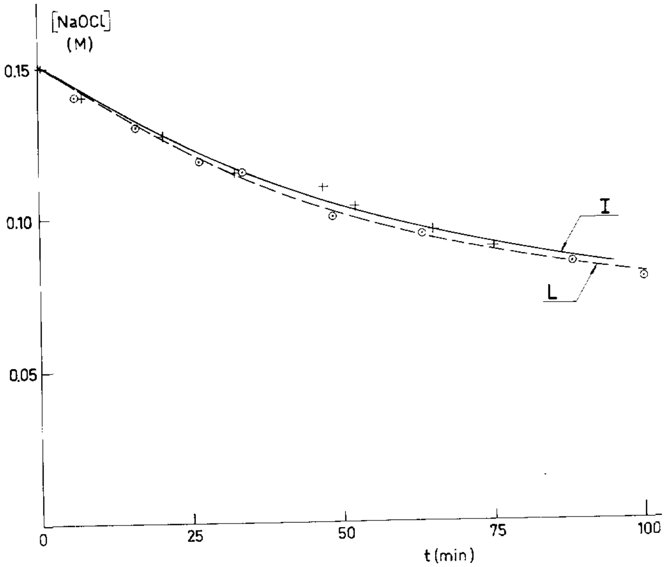


Fig. 4b. Comparison of the reactivity of amylodextrins and inulin in the oxidation with hypochlorite (C = 0.15 M) at pH 8.0 and 25 ° C.

Kinetics of the oxidation of inulin and model calculations

In Figures 5-12 the profiles (curves E) of the hypochlorite/ hypochlorous acid consumption in the oxidation of inulin at pH values between 6.5 and 8.0 and at different oxidant concentrations are presented. In these Figures we present also the calculated profiles for the three reactions R, Q and S. In Figures 13-15 the experimental results of *Floor* et al. [11] in the oxidation of starch at pH 8, 8.5 and 9 are shown, together with the results of the calculation.

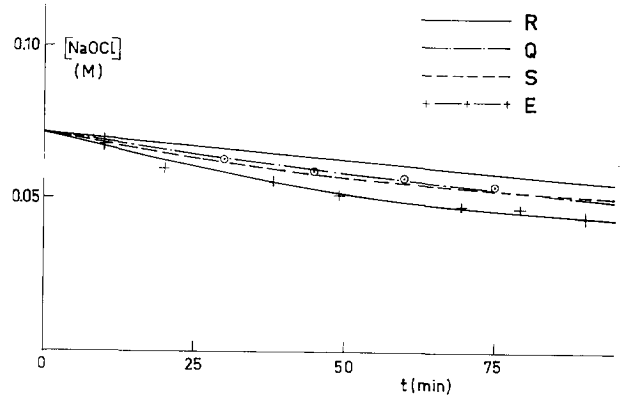


Fig. 5. Consumption of HOCl/OCl⁻ (C = 0.07 M) as a function of time in the oxidation of inulin at pH 6.5 and 25 °C (curve E) and comparison with calculated profiles for reactions Q, R and S.

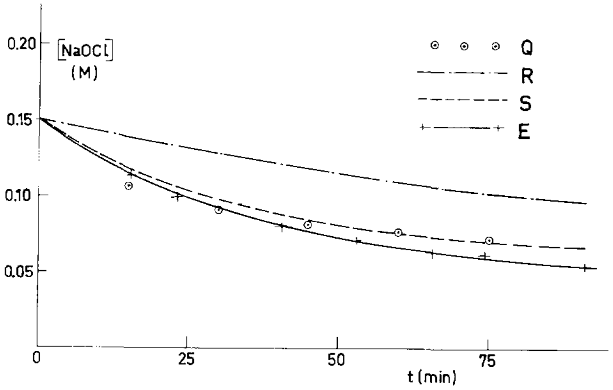


Fig. 6. Consumption of HOCl/OCl⁻ (C = 0.15 M) as a function of time in the oxidation of inulin at pH 6.5 and 25 °C (curve E) and comparison with calculated calculated profiles for reactions Q, R and S.

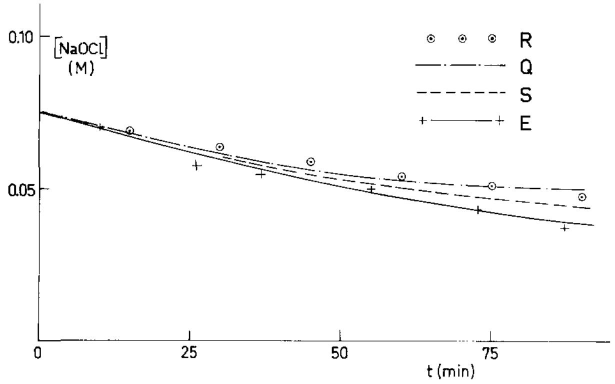


Fig. 7. Consumption of HOCl/OCl⁻ (C = 0.07 M) as a function of time in the oxidation of inulin at pH 7.0 and 25 °C (curve E) and comparison with calculated profiles for reactions Q, R and S (line through circles not drawn).

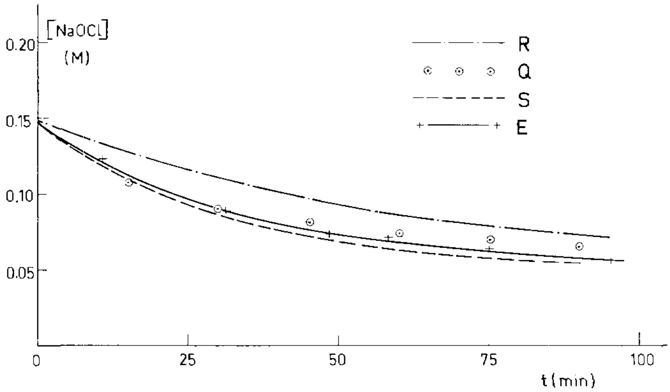


Fig. 8. Consumption of HOCl/OCl⁻ (C = 0.15 M) as a function of time in the oxidation of inulin at pH 7.0 and 25 °C (curve E) and comparison with calculated model profiles for reactions Q, R and S (line through circles not drawn).

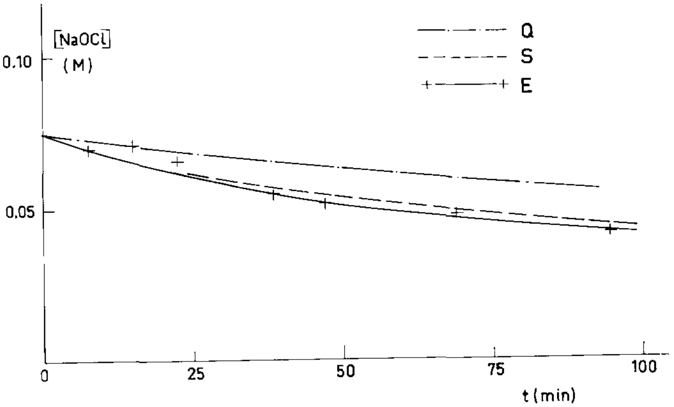


Fig. 9. Consumption of HOCl/OCl⁻ (C = 0.07 M) as a function of time in the oxidation of inulin at pH 7.5 and 25 °C (curve E) and comparison with calculated profiles for reactions Q, R and S (line of reaction R coincides with experimental line E).

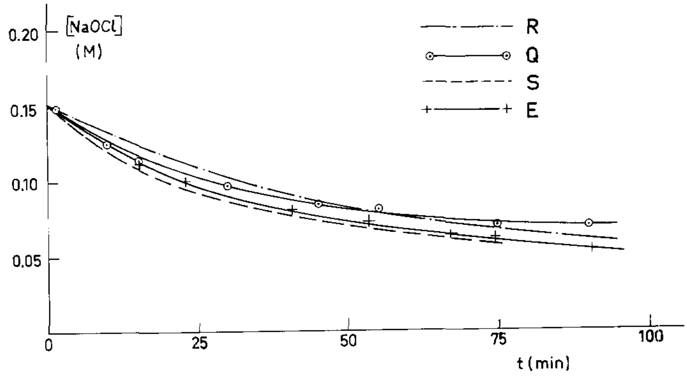


Fig. 10. Consumption of HOCl/OCl⁻ (C = 0.15 M) as a function of time in the oxidation of inulin at pH 7.5 and 25 °C (curve E) and comparison with calculated profiles for reactions Q, R and S (line through circles not drawn).

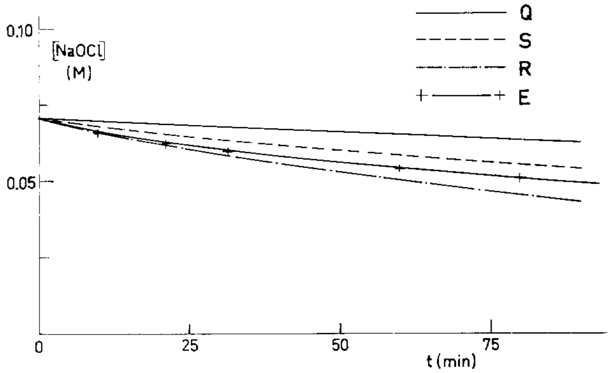


Fig. 11. Consumption of HOCl/OCl⁻ (C = 0.07 M) as a function of time in the oxidation of inulin at pH 8.0 and 25 °C (curve E) and comparison with calculated profiles for reactions Q, R and S.

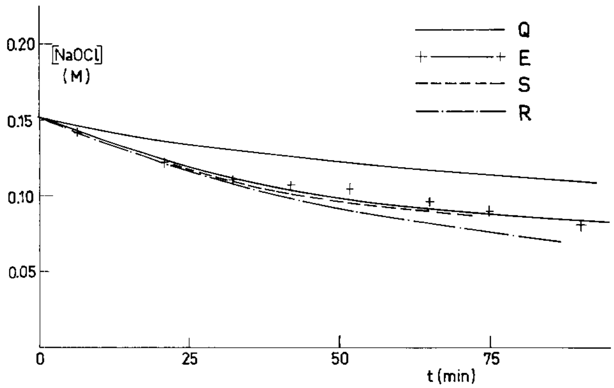


Fig. 12. Consumption of HOCl/OCl⁻ (C = 0.15 M) as a function of time in the oxidation inulin at pH 8.0 and 25 °C (curve E) and comparison with calculated profiles for reactions Q, R and S.

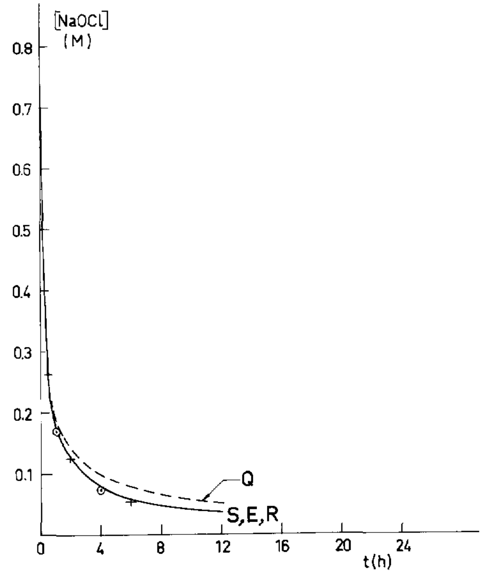


Fig. 13. Consumption of HOCl/OCl⁻ (C = 0.75 M) as a function of time in the oxidation of starch at pH 8.0 and 20 °C (curve E) and comparison with calculated model reactions R, Q and S..

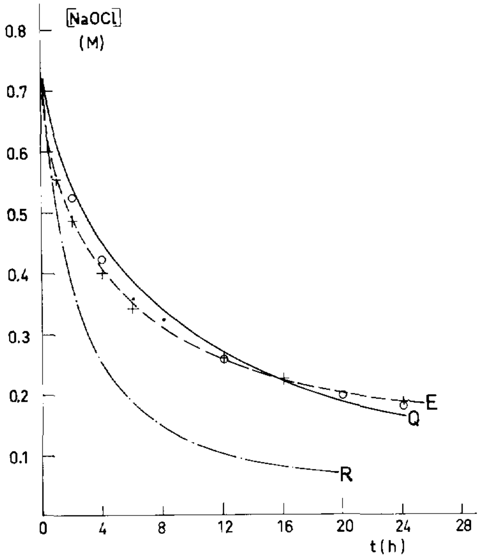


Fig. 14. Consumption of HOCl/OCl⁻ (C = 0.75 M) as a function of time in the oxidation of starch at pH 8.5 and 20 °C (curve E) and comparison with calculated model reactions R, Q and S (line through circles (S) is not drawn).

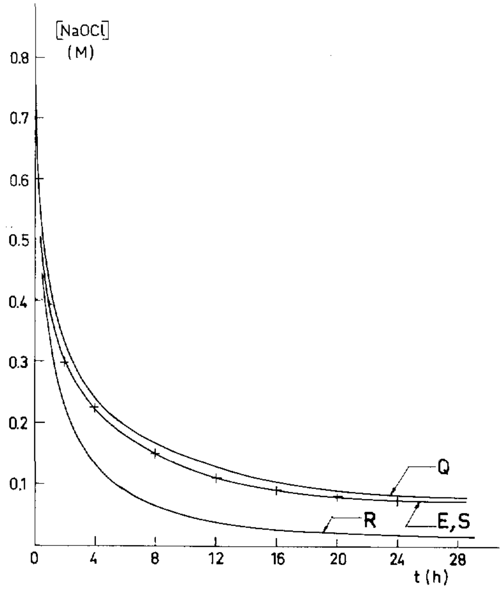


Fig. 15. Consumption of HOCl/OCl⁻ (C = 0.75 M) as a function of time in the oxidation of starch at pH 9.0 and 20 °C (curve E) and comparison with calculated model reactions R, Q and S (line S coincides with experimental curve S).

The results of an experiment with high inulin concentration are given in Fig 16. In spite of the high substrate concentration the reactivity seems to be the same as seen in an experiment carried out at the same conditions with a low substrate concentration (see Fig. 10), in agreement with the assumption that the reaction of inulin with HOCl/OCl⁻ is not rate determining.

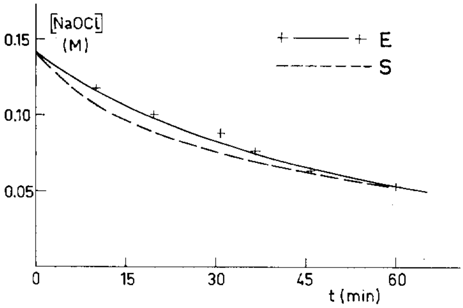


Fig. 16. Consumption of HOCl/OCl⁻ (C = 0.14 M) as a function of time in the oxidation of inulin at pH 7.5 and 25 °C (curve E) and comparison with calculated profile for reaction S.

Reactivity of cyclohexanediol isomers and 1,2-cyclohexanedione

In Fig. 17 the results of the experiments carried out with the cyclohexanediol isomers are shown. It appears that *trans*-1,2-cyclohexanediol is the most reactive of the isomers. Because the reactivity of the *primary products of these compounds* towards hypochlorite is unknown a comparison may be premature.

It was observed that 1,2-cyclohexanedione is very reactive; under the conditions as described above the hypochlorite was consumed within 10 seconds. It was also seen that the extent of acid formation from 1,3- and 1,4-cyclohexanediol was much less than from 1,2-cyclohexanediol.

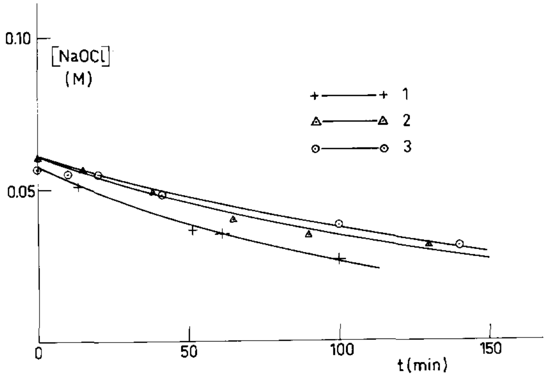


Fig. 17. Consumption of HOCl/OCl⁻ (C = 0.07 M) as a function of time in the oxidation of cyclohexanediol isomers at pH 7.0 and 25 °C. 1 = trans-1,2-cyclohexanediol, 2 = 1,3-cyclohexanediols, 3 = 1,4-cyclohexanediols.

Computer modelling study and discussion

General remarks

For the computer modelling of the oxidation process the PC version of the computer program "Facsimile" was used (software developed by IAEA, Harwell, UK). The main objective of this exercise was to investigate whether the first step in the hypochlorite oxidation is rate determining and which set of reactions describes the processes in the best way. Because of the unknown mechanisms and rate constants, several assumptions had to be made. For some rate constants it appeared possible to estimate or derive them from experimental data.

Reaction scheme

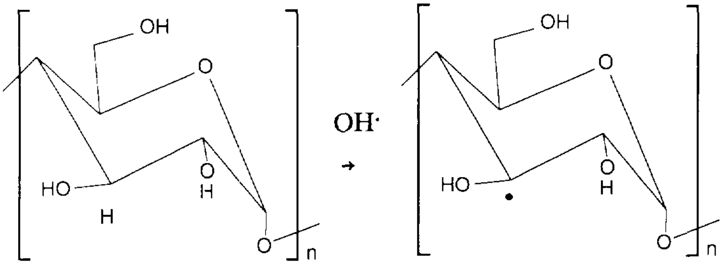
In the hypochlorite oxidation of glucans or fructans four groups of reactions can be distinguished:

a. the carbohydrate conversion
b. the hypochlorite decomposition (chlorate formation)
c. the reaction of HOCl with OCl^-
d. miscellaneous reactions.

a. the carbohydrate conversion

In the oxidation of cellulose with sodium hypochlorite it has been postulated that radicals and/or atoms arise from the reaction of OCl^- and HOCl [13-15]. In view of the reactive character of such species we have assumed that this reaction is rate determining, which is also suggested by the fact that, as noted above, the reactivity of starch and inulin in this system is very similar and by the fact that the rate does not seem to depend on the substrate concentration.
For simplicity the reactions have been formulated in such a way that hydroxyl radicals arise[1]. Of course other reactive species can be postulated e.g. the formation of $Cl^\cdot$, $ClO^\cdot$ and Cl_2O_2 cannot be excluded. However, the results of the simulation will be similar.

The first step in the glycolic oxidation of dextrins is supposed to proceed as follows:



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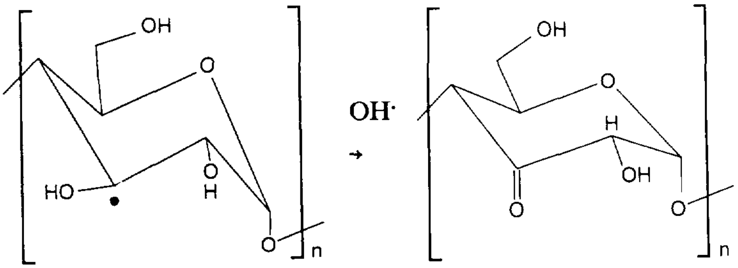
[1] Hydroxyl radicals play in many processes an important role e.g. the degradation of organic compounds in the atmosphere and in combustion (*cf.*also the Annex of this chapter).

The intermediate reacts according to



The first step may also proceed in another way, but with the same net result. For inulin a similar first step is formulated for the C_3,C_4-moiety of the furanose unit. It is assumed that a fast reaction occurs between the intermediate products and NaOCl or HOCl (reaction 3 and 4). Evidence for this follows from the results of .experiments of *Floor* et al. [11], from our results described elsewhere (chapter 6), and from the observation that 1,2-cyclohexanedione is very reactive towards hypochlorite. Beside the oxidation by the hypothetical species (the-OH radical), reaction 1-4, the reactions of the carbohydrate with HOCl and OCl^- have to be considered (reaction 5 and 6). From the investigations of *Patel* et al. [17, 18] and *Schmorak* et al. [19] it follows that at low pH and high pH reactions occur with respectively HOCl and OCl^-. The (second-order) rate constants which are used in this model are derived from the (first-order) rate constants mentioned in these studies. The reactions concerning the glycolic oxidation of the carbohydrates are summarized in Scheme 1.

Scheme 1. Reactions of substrate and intermediate products [1]

1. ld + $OH^\cdot$ → ldri + H_2O
2. ldri + $OH^\cdot$ → ldr1 + H_2O
3. ldr1 + HOCl → ldr2 + H_2O + HCl
4. ldr2 + HOCl → dcl + HCl
5. ld + HOCl → ldr1 + H_2O
6. ld + OCl^- → ldr1 + H_2O

---

[1] Abbrevations: ld = linear dextrins; ldri = first intermediate (radical) ; ldr1 = stable (mono) carbonyl compound; ldr2 = dicarbonyl compound ; dcl = dicarboxy-linear dextrins.

b. the hypochlorite decomposition

It is well-known that OCl^- and HOCl may decompose resulting in the formation of chlorate. Sodium chlorite reacts with sodium hypochlorite, also resulting in the formation of chlorate [26].
Because of the pH dependence of these reactions we have assumed that they proceed in a similar way as the carbohydrate oxidation i.e. the reactive species reacts with hypochlorous acid. A survey is given in Scheme 2.

Scheme 2. Reactions leading to chlorate (group b)

7. $HOCl + OH^\cdot \rightarrow ClO^\cdot + H_2O$
8. $ClO^\cdot + HOCl \rightarrow HClO_2 + Cl^\cdot$
9. $2\,Cl^\cdot \rightarrow Cl_2$
10. $HOCl + HClO_2 \rightarrow HClO_3 + HCl$

The rate constants of this group have been fitted using the data given by *Whistler* et al. [4]. These authors oxidized amylopectin with sodium hypochlorite at various pH and hypochlorite concentrations and analyzed for the chlorate formation. The results are summarized in Table 1. A close approximation of the chlorate formation could be obtained at pH 7. At pH 5 and 9 a difference is seen, but the trend in chlorate formation is similar to the results of *Whistler* et al. [4].

Table 1. Chlorate formation from hypochlorous acid and hypochlorite at various pH [4].

pH	3	5	7	9	10.5	12
% chlorate (exp.)	1.5	7.1	28.8	4.6	0.7	0.5
% chlorate (calc.)	-	9.5	31.0	3.0	0.3	-

c. reactions of HOCl and OCl^- (radical production)

As mentioned above *Singh* [14], *Nevell* and *Singh* [15] and *Epstein* and *Lewin* [13] have considered various reactions which might be responsible for the production of radicals/atoms.

The reactions which have been proposed, are included separately in the respective scenarios (see Scheme 3). Because of the reactivity of the radical type species the reaction in which it is generated, is considered to be rate determining.

Scheme 3. Reactions of HOCl and OCl⁻ [1]

11a. (Q) $3HOCl + OCl^- \rightarrow 2\ OH^\cdot + OCl^- + 2Cl_2$

11b. (S) $2HOCl + OCl^- \rightarrow 2\ OH^\cdot + OCl^- + Cl_2$

11c. (R) $HOCl + OCl^- \rightarrow 2\ OH^\cdot + OCl^- + HCl$

It is clear that the pH dependence on the rate in the hypochlorite/hypochlorous acid oxidation can be explained by the $HOCl/OCl^-$ ratio.

ad 11a.

The reaction rate (for d[HOCl]/dt)

$$- d[HOCl]/ dt = k\ [HOCl]^{3/2}.\ [OCl^-]^{1/2}$$

neglecting the contribution of reactions 5 and 6, mentioned in Scheme 1. Because
$[HOCl(t)] = [HOCl] + [OCl^-]$
and

$$K_a = [H^+].[OCl^-]/[HOCl]\ ^2$$

the equation given above can be rewritten:

$$-d[HOCl]/dt = k[HOCl(t)].K_a.[H^+]^{3/2}/([H^+] + K_a)^{5/2}.$$

The maximum rate is found at $[H^+] = 3K_a$, i.e pH = 7.00.

ad 11b.

The reaction rate is given by
$-d[HOCl]/dt = k\ [HOCl]^1.\ [OCl^-]^{1/2}.$

---

[1] The exact stoichiometry of these reactions is unknown; H_2O is assumed to be involved .

[2] $pK_a = 7.48$.

neglecting the contribution of reactions 5 and 6.

The pH optimum is now found at pH = 7.18 ($[H^+] = 2\ K_a$).

ad 11c.
The reaction rate is given by

$$-\ d[HOCl]/dt = k\ [HOCl]^{1/2}.\ [OCl^-]^{1/2}$$

neglecting the contribution of reactions 5 and 6.

In this case the pH optimum is found at pH = 7.48 ($[H+] = K_a$).

d. miscellaneous reactions

In Scheme 4 the equilibrium reactions of Cl_2, HOCl and OCl^- and a termination reaction are given.

Scheme 4. Miscellaneous reactions

12. $HOCl \rightleftharpoons H^+ + OCl^-$

13. $Cl_2 + H_2O \rightleftharpoons HOCl + HCl$

14. $2\ OH^\cdot \rightarrow H_2O_2$

Approach and method of the modelling study

As mentioned above the production of radicals is supposed to be the rate determining step. The first step in our approach was to fit the chlorate formation (experiments of *Whistler* et al.) and to fit the experiments of *Floor* et al. with respect to the hypochlorite consumption (oxidation of starch at pH 8). An important factor is the ratio of the rate constants of reaction 1 and 7. Once a set of variables (rate constants) in one experiment was chosen the other experiments were calculated with this values.

The results of the calculations are presented in the Figures 5-15, together with the experimental data.

The complete scheme of the reactions and their respective rate constants are given in Table 2. For the abbreviations used, see footnote [1], page 78.

Table 2. Survey of the reactions included in the computer simulation.

Reaction	k^1
1. ld + $OH^{\cdot}$ → ldri + (H_2O)	2. 10^{7}
2. ldri + $OH^{\cdot}$ → ldr1 + (H_2O)	1. 10^{10}
3. ldr1 + $HOCl$ → ldr2 + (H_2O) + HCl	6. 10^{-2}
4. ldr2 + $HOCl$ → dcl + HCl	6. 10^{-2}
5. ld + $HOCl$ → ldr1 + H_2O + HCl	1.4. 10^{-4}
6. ld + OCl^- → ldr1 + H_2O + HCl	4. 10^{-5}
7. $HOCl$ + $OH^{\cdot}$ → $HClO_2$ + $Cl^{\cdot}$	9. 10^{7}
8. $HClO_2$ + $HOCl$ → $HClO_3$ + HCl	2
9. $2Cl^{\cdot}$ → Cl_2	1. 10^{11}
10. $HOCl$ + $HClO_2$ → HCl + $HClO_3$	2
11a. $3HOCl$ + OCl^- → 2 $OH^{\cdot}$ + OCl^- + Cl_2 + HCl	0.64
11b. $2HOCl$ + OCl^- → 2 $OH^{\cdot}$ + OCl^- + Cl_2	4.6. 10^{-3}
11c. $HOCl$ + OCl^- → $2OH^{\cdot}$ + OCl^- + HCl	1.6 . 10^{-4}
12. $HOCl$ ⇌ H^+ + OCl^-	eq.
13. Cl_2 + H_2O ⇌ $HOCl$ + HCl	eq.
14. 2 $OH^{\cdot}$ → H_2O_2	1. 10^{11}

[1] *Units are in* s^{-1}, $M^{-1}.\ s^{-1}$, $M^{-2}.\ s^{-1}$ *or* $M^{-3}.\ s^{-1}$.

Discussion and conclusions

The reactivity of inulin and dextrins appears to be similar in the pH range 6.5-8.0 which suggests that the reactivity of the system is not determined by the reactivity of the substrate but dominated by reaction 11, the formation of a reactive species from HOCl and OCl^-. Supporting evidence is found in the fact that the highest oxidation rate in the oxidation of starch, dextrins and inulin is found approximately at pH 7, in agreement with the results of other authors, who investigated the oxidation of cellulose and amylopectin.

Computer model calculations including the supposed rate determining reactions allow to make a comparison over a wide pH range. A summary of the simulation and the experimental results and a qualification is given in Table 3.

Table 3. Comparison of the results of the experimental and calculated hypochlorite concentrations.

Experiment (See Figure)	pH	$C_{carbohydrate}$ (M)	C_{HOCl} (M)	Reaction Q	Reaction R	Reaction S
4	6.5	0.113	0.07	±	\	±
5	6.5	0.113	0.15	±	\	a
6	7.0	0.113	0.075	\	\	±
7	7.0	0.113	0.15	±	\	a
8	7.5	0.113	0.075	\	a	a
9	7.5	0.113	0.15	\	\	±
10	8.0	0.113	0.07	\	/	±
11	8.0	0.113	0.15	\	/	a
12	8.0	0.25	0.75	\	a	a
13	8.5	0.25	0.75	\	/	a
14	9.0	0.25	0.75	±	/	a

a = agreement between experimental and predicted (calculated) values.
± = *reasonable fit.*
\ = *predicted reaction too slow.*
/ = *predicted reaction too fast.*

It can be seen that in the range pH 6.5-7.0 the experimental and calculated values agree well for reaction Q which, in view of the pH optimum of 7 of this reaction, is not surprising. At pH 7.5 and especially pH 8.0 relatively large differences between measured and calculated values can be seen. For scenario R, whose pH optimum is at 7.48 the best agreement is seen at pH between 7 and 8, whereas a significant difference is observed at pH 6.5. Also at higher pH differences are seen.

A remarkable fact is that for reactions Q and R at a given pH only at one concentration level agreement between calculated and measured results is observed. By contrast it is seen that scenario S gives the best results

- in the pH range 6.5-9.0
- for all concentrations examined
- with *Floor's* experiments.

This indicates that the order of the formation reaction of the reactive species is predicted in the right way by scenario S.

It can be concluded that a tool is available for the calculation/prediction of the course of the reaction of carbohydrates with hypochlorous acid/hypochlorite and its pH dependence. However, as the formation of radicals has not been proven and also the suggested structures and reactions of the intermediate carbohydrate structures remain unknown, further studies are needed to elucidate the mechanisms.

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CHAPTER 4

ANNEX

On the selectivity and the mechanism of the hypochlorite oxidation of carbohydrates

The mechanism of the hypochlorite oxidation of carbohydrates is unknown. Especially intriguing within the scope of the present study is the mechanism which should explain the selectivity of the oxidation of the glycol moiety of the glucose unit in starch compared to C_6-oxidationand to oxidation at C_1 and at C_4 assumed to induce depolymerization in 1,4-glucans similarly. In inulin glycolic oxidation at C_3-C_4 has to be compared with oxidation of the primary alcohol group (at C_6)and with ether type CH- and CH_2-groups at C_1 and C_5respectively.

In the foregoing chapter evidence was presented that a radical mechanism may be responsible for the reaction of hypochlorous acid/hypochlorite with carbohydrates. Although the nature of the active species as yet remains unidentified, one can speculate about the consequences of a radical behaviour. We have indicated that several species may arise: O- and Cl-atoms as well as ClO- and OH-radicals.

Especially with respect to the reactivity of OH-radicals much knowledge is available [1-4], due to their important role in many processes (atmospheric degradation of organic compounds, combustion). An important conclusion from the numerous studies is that the reactivity of organic molecules of various classes towards the OH-radical can be predicted in a reasonably accurate way. Moreover it was established that there is a

correlation between the reactivity of organic compounds in the atmosphere and in water [5].
It is therefore tempting to make an estimate of the relative reactivity of the structural parts of a glucose and a fructose moiety in, respectively, starch and inulin and to see whether a selectivity towards glycolic oxidation is to be expected.

The rate constants of most classes of compounds in which OH-radicals participate, can be predicted on the basis of some empirical rules:

1. each structural feature contributes to a certain part to the overall reactivity of a molecule and has its own basic reactivity

2. the reactivity of each structural feature is influenced in a positive or negative way by the adjacent structural parts

3. electron donating substituents enhance the reactivity whereas electron withdrawing groups generally diminish the reactivity.

In Table 1 the experimental rate constants of the homologous series of the n-alkanes are given [4]. Also included in this table are the calculated reactivities and the reactivities of the structural parts of these molecules as estimated by the present author [6] and the overall reactivity being the sum of k_{OH} of the structural parts.

The main empirical rules for the estimation of the reactivity of the structural parts are as follows:

a. the reactivity of a methyl group (in ethane) is $0.14.10^{-12} cm^3.molecule^{-1}. s^{-1}$, which means for the k_{OH} of each H-atom $0.047.10^{-12} cm^3.molecule^{-1}. s^{-1}$
b. the reactivity of a methyl group increases with increasing number C-atoms of the adjacent alkyl group (10% per C-atom with a maximum effect of 45% by 4 C-atoms)
c. the basic reactivity of the methylene group (as follows from the reactivity of propane) is $1.0.10^{-12} cm^3.molecule^{-1}. s^{-1}$,or $0.5.10^{-12} cm^3.molecule^{-1}. s^{-1}$ for each CH-bond. The reactivity of the methylene group increases with increasing number of the C-atoms of the adjacent alkyl group (10% per alkyl group and 10% per C-atom).

Table 2 gives experimental and calculated data for some branched aliphatic hydrocarbons [4].

Table 1. Overall and regio reactivities of linear aliphatic hydrocarbons towards OH-radicals.

Compound	k_{OH} (exp.)	k_{OH} (calc.)	k_{CH3}	k_{CH2} (2)	k_{CH2} (3)	k_{CH2} (4, 5, 6)
Methane	0.01	-	-	-	-	-
Ethane	0.28	-	0.14	-	-	-
Propane	1.15	1.30	0.15	1.00	-	-
Butane	2.53	2.54	0.17	1.10	-	-
Pentane	4.00	3.78	0.18	1.10	1.22-	-
Hexane	5.58	5.42	0.18	1.21	1.32	-
Heptane	7.20	6.88	0.18	1.21	1.33	1.44
Octane	8.72	8.32	0.18	1.21	1.33	1.44
Nonane	10.0	9.76	0.18	1.21	1.33	1.44
Decane	11.2	11.2	0.18	1.21	1.33	1.44
Undecane	13.3	12.6	0.18	1.21	1.33	1.44
Dodecane	13.9	14.1	0.18	1.21	1.33	1.44
Tridecane	15.5	15.5	0.18	1.21	1.33	1.44

1 Units are in cm^3. $molecule^{-1}$. s^{-1}. 10^{-12}. Between brackets the position of the methylene group in the molecule is given. The symmetry of the molecule is taken into account.

The rules for the calculation of the k_{OH} for branched aliphatic hydrocarbons are similar to those for the unbranched compounds.

a. the basic reactivity of the tertiary CH-group is $1.86.10^{-12} cm^3.molecule^{-1}. s^{-1}$.
b. replacement of a methyl- by an ethyl group gives per replaced methyl group 20% increase in reactivity.
The reactivity of the CH group increases with increasing number of the C-atoms of the adjacent alkyl group (10% per alkyl group and 10% per C-atom), with a maximum of 3 C-atoms.

Table 2. Overall and estimated regio reactivities of branched aliphatic hydrocarbons towards OH-radicals.

Compound	k_{OH}[1] (exp.)	k_{OH} (calc.)	k_{CH3}	k_{CH2}	k_{CH2}	k_{CH}
2-Methylpropane	2.37	2.37	0.17	-	-	1.86
2-Methylbutane	3.90	3.99	0.18	1.22	-	2.23
2,2-Dimethylpropane	0.87	0.76	0.19	-	-	-
2-Methylpentane	5.5	5.77	0.18	1.33	1.44	2.46
3-Methylpentane	5.6	5.80	0.18	1.33	1.33	2.60
2,2-Dimethylbutane	2.6	2.05	0.18	1.33	-	-
2,3-Dimethylbutane	6.2	5.60	0.18	-	-	2.44
2,4-Dimethylpentane	5.1	7.44	0.18	1.44	-	2.64
2,2,3-Trimethylbutane	4.1	3.56	0.18	-	-	2.46
2,2,4-Trimethylpentane	3.66	5.33	0.18	1.50	-	2.93
2,2,3,3-Tetramethylbutane	1.06	1.08	0.18	-	-	-

[1] *Units are in* $cm^3.molecule^{-1}.\ s^{-1}.\ 10^{-12}$.

From Table 1 and 2 it can be seen that there is a good agreement between measured and predicted values[1]. The order of reactivity of primary : secondary : tertiary CH-groups towards the OH-radical is 0.05 : 0.7 : 1.86 = 1 : 14 : 37.

Table 3 gives data of the reactivity of various alkenes towards the OH-radical [1-4]. It is important to note that in the reaction of saturated hydrocarbons with OH-radicals abstraction occurs, whereas in the reaction of alkenes and also of the aromatic hydrocarbons addition of OH-radicals to the unsaturated part is the predominant pathway.

The rules for the calculation of the reactivity of alkenes are:

a. the basic reactivity of C=C (addition) is $8.5.10^{-12} cm^3.molecule^{-1}.\ s^{-1}$

---

[1] In a few cases the observed reactivity is lower, which is possibly due to steric hindrance of the most reactive part of the molecule.

b. replacement of a hydrogen atom attached to the double bond by a methyl group increases the reactivity of the double bond with a factor 3. Each extra carbon leads to a further increase with 10%
c. two geminal methyl groups at the double bond (as in isobutene) increase the reactivity by a factor 6
d. two methyl groups attached to the double bond with a (Z)-configuration increase the reactivity of the double bond by a factor 6.6
e. two methyl groups attached to the double bond with an (E) - configuration increase the reactivity of the double bond by a factor 7.2
f. if one of the methyl groups in any of these configurations is replaced by an alkyl group the reactivity of the double bond increases with 10% per C-atom of the alkyl group. The maximum effect is given by 3 C-atoms
g. the aliphatic part contributes to the reactivity according the rules given for the aliphatics given above.

It has been recognized that the reactivity of an α-methyl- or methylene group (with allylic hydrogen atoms), should be much higher than the reactivity of such groups in a aliphatic molecule. *Atkinson* et al. discussed [2] the results of several investigators, who studied the product formation of propene. It appeared from the most reliable study that OH-radical addition to ethene is the exclusive reaction pathway and OH-radical addition to propene is by far the predominant pathway [2]. This might also be true for the reactions of the OH-radical with the other methyl substituted ethenes. On the other hand *Atkinson* et al. postulated from their own study that the CH_2- and CH-group in butene and 3-methyl-1-butene may contribute significantly to the overall reactivity (per allylic C-H bond $5.10^{-12} cm^3.molecule^{-1}. s^{-1}$) . However, experimental support of this hypothesis is lacking. In a later paper these authors state that the contribution of the abstraction pathway for propene is < 2% and in 1-butene < 10% [4]. From this statement upper limits for the reactivity of the methyl group and of the α-methylene group can be derived (0.4 and $3.10^{-12} cm^3. molecule^{-1}. s^{-1}$, respectively). If the reactivity of the α-methylene or tertiary CH-group is assumed to be $4.10^{-12} cm^3. molecule^{-1}. s^{-1}$ a good agreement between measured and calculated values is obtained.

In view of the extended data base one has to conclude that indeed the abstraction pathway, contrary to the expectation, contributes only to a minor extent in the overall reactivity of alkenes towards OH-radicals.

The relatively small importance of the abstraction pathway is apparent from the reactivity of aromatic hydrocarbons [2, 4]. In these reactions the formation of benzylic structures is expected. However, the reactivity of the aliphatic parts is only slightly higher than in the corresponding aliphatic compounds.

Table 3. Overall and estimated regio reactivities of unsaturated hydrocarbons towards OH-radicals.[1]

Compound	k_{OH}(exp.)	k_{OH} (calc.)	$k_{C=C}$	$k_{aliphatic}$[2]
Ethene	8.5	-	8.5	-
Propene	26.3	25.7	25.5	0.2
1-Butene	31.4	31.6	27.4	4.2
1-Pentene	31.4	37.1	30.9	6.2
1-Hexene	37.0	39.1	30.9	8.2
1-Heptene	40.0	41.1	30.9	10.2
Isobutene	51.4	51.4	51.0	0.4
3-Methyl-1-butene	31.8	35.3	30.9	4.4
2-Methyl-1-butene	60.7	58.4	54.0	4.4
2-Methyl-1-pentene	62.6	62.7	56.3	6.4
(Z)-2-Butene	56.1	56.5	56.1	0.4
(E)-2-Butene	63.7	61.6	61.2	0.4
(Z)-2-Pentene	65.1	63.3	58.9	4.4
(E)-2-Pentene	67.0	68.7	64.3	4.4
(E)-4-Methyl-2-pentene	60.8	71.9	67.3	4.6
2-Methyl-2-butene	86.9	84.8	84.2	0.6
2-Methyl-2-pentene	88.8	91.2	87.0	4.2

[1] *Units are in* $cm^3.molecule^{-1}.\ s^{-1}.\ 10^{-12}$.

[2] *For the aliphatic parts fixed values are used as an approximation i.e* $k_{CH3} = 0.2\ .\ 10^{-12}\ cm^3.molecule^{-1}.\ s^{-1}.\ 10^{-12}$, $k_{CH2} = 2.0\ cm^3.molecule^{-1}.\ s^{-1}.\ 10^{-12}$. *The reactivity of an α-methylene group is taken as* $4.0.10^{-12} cm^3.molecule^{-1}.\ s^{-1}$ *(see text).*

The reactivity of other important chemical classes e.g. alcohols, aldehydes, esters, ketones and halogenated hydrocarbons can be predicted on the basis of chemical knowledge and empirical rules too [1-4, 6]. With respect to the estimation of the reactivity of carbohydrates and derivatives alcohols, ethers and acetals/ketals are of importance. In Table 4 a survey of the rate constants of some alcohols is presented [4, 8-10].

Table 4. Reactivity of alcohols towards the OH-radical.

Compound	k_{OH} (exp.)	k_{OH} (calc.)	k_{CH3}	$k_{CH2/CH}$	k_{CHOH}
Methanol	1.0	-	-	-	-
Ethanol	2.9	3.2	0.2	-	3.0
1-Propanol	4.8	5.6	0.2	1.5	3.9
1-Butanol	7.3	8.1	0.2	1.5	4.9
1-Pentanol	10.5	9.6	0.2	1.5	4.9
1-Hexanol	12.4	11.1	0.2	1.5	4.9
1-Heptanol	13.6	12.6	0.2	1.5	4.9
2-Propanol	6.2	6.4	0.2	-	6.0
t-Butanol	0.6	0.6	0.2	-	-
3-Methyl-2-butanol	12.4	10.7	0.2	2.0	8.1
2-Pentanol	11.8	11.3	0.2	1.5	8.1
3-Pentanol	12.2	12.8	0.2	1.5	9.6
2-Hexanol	12.4	13.0	0.2	1.5	8.1
Ethylene glycol	7.7	7.7			3.85
1,2-Propanediol	12.0	12.0	0.2		7.0; 4.8[2]

[1] *Units are in $cm^3.molecule^{-1}. s^{-1}. 10^{-12}$.*

[2] *Reactivity of the secondary and primary alcohol group, respectively.*

The rules we extract for the prediction of the reactivity of alcohols are:

1. the basic reactivity of the CHOH-group (in methanol) is $1.0.10^{-12}cm^3.molecule^{-1}. s^{-1}$ i.e. each C-H bond contributes $0.33.10^{-12}cm^3.molecule^{-1}. s^{-1}$.
2. replacement of a hydrogen atom by methyl leads to an increase in reactivity by a factor of 3, i.e. each C-H bond contributes $1.5.10^{-12}cm^3.molecule^{-1}. s^{-1}$.

3. upon increasing number of C-atoms of the alkyl group the factor further increases with 30% for each C-atom (maximum by 3 atoms)[1].
4. the reactivity of the (sec.) CHOH group is $6.0.10^{-12}cm^3.molecule^{-1}. s^{-1}$ (activation of the CHOH group by two methyl groups). The extra activation is calculated according rule 3.

Of special interest for the estimation of the reactivity of the vicinal diol unit of the anhydroglucose and -fructose unit in starch and inulin, respectively are 1,2-ethanediol and 1,2-propanediol, the only two diol compounds for which the rate constants are known. The rate constant of 1,2-propanediol is $12.10^{-12} cm^3. molecule^{-1}. s^{-1}$.The reactivity of ethanol is $2.9.10^{-12}cm^3.molecule^{-1}. s^{-1}$ whereas that of 1,2-ethanediol is $7.7.10^{-12}cm^3. molecule^{-1}. s^{-1}$, which makes clear that the influence of a CH_2OH-group exceeds that of a methyl group with about 33%.

Since the CH_2OH-group is *extra* activated by the *extra* C atoms it can be derived that the reactivity of the (sec.) CHOH-group in 1,2-propanediol is $7.0.10^{-12}cm^3.molecule^{-1}. s^{-1}$.

Other parts of the glucose and fructose moiety are also reactive. These concern acetal/ketal and ether functions. From literature data it is known that ethers, acetals and ketals are, as expected, more reactive than the corresponding alkanes. For instance the reactivity of diethyl ether is much higher than that of n-pentane (see Table 1 and 6). Data about the k_{OH} of some ethers, ketals and acetals are given in Table 5.

Empirical rules are not so easy to derive because of the long range effect of the O-atom on all CH_2-or tertiary CH-groups [9]. It has been noted that each CH_2-group in ethers seems to contribute $4.5.10^{-12}cm^3.molecule^{-1}. s^{-1}$ to the overall reactivity, which would imply that the reactivity of each methylene group is three times higher than in alkanes.

The structural feature of the acetal and ketal C-H groups as occurring in the glucan- and fructan-moiety are found in some simple molecules. The structural acetal feature at C_1 in starch occurs in 1,1-dimethoxyethane and 1,1,3-trimethoxypropane. By comparison of the reactivities of the various parts of the respective moieties the reaction constants are estimated.

The reactivity of C_1 in 1,1-dimethoxyethane (DME) can be calculated as follows:
$C1 = k_{DME} - k_{methyl} - 2k_{methoxy}$ $(8.9 - 0.2 - 3.5 = 5.2.10^{-12}cm^3.molecule^{-1}. s^{-1})$.

---

[1] The reaction of alcohols at the CHOH group proceeds mainly via abstraction of the H-atom attached to the C-atom

$$R_2CHOH + OH \rightarrow R_2C^{\cdot}OH + H_2O.$$

The reactivity of C_4 in starch, the structural feature CH, can be derived in a similar way. This feature is found in an ether derived from a secondary alcohol (1,2-dimethoxypropane and diisopropyl ether).
The reactivity of C_5 can be derived from diisopropyl ether.
In Table 5 a survey of the reactivity of various structural features is given.

Table 5. Reactivity of some ethers, acetals and ketals towards the OH-radical.

Compound	k_{OH} (exp.)	Structural feature	k_{OH}
Dimethyl ether	3.5	OCH_3	1.75 (OCH_3)
n-Butyl methyl ether	16.4	$O(CH_2)_3$	4.8 (CH_2)
t-Butyl methyl ether	2.64	OCH_3	1.75 (OCH_3)
Diethyl ether	9.2	OCH_2	4.3 (CH_2)
Di-n-propyl ether	20.3	OCH_2CH_2	4.9 (CH_2)
Di-n-butyl ether	27	$OCH_2CH_2CH_2$	4.4 (CH_2)
Di-n-pentyl ether	34	$OCH_2CH_2CH_2CH_2$	4.2 (CH_2)
n-Butyl ethyl ether	22.8	$OCH_2CH_2CH_2$, OCH_2	4.5 (CH_2)
Diisopropyl ether	10.7	$OCH(CH_3)_2$	4.8 (OCH)
1,3,5-Trioxane	6.71		
1,2-Dimethoxypropane	14.3	$RCHOCH_3$	4.7 (OCH)
2,2-Dimethoxypropane	3.9	OCH_3	
1,1-Dimethoxyethane	8.9	OCH	5.2 (OCH)
2,2-Diethoxypropane	11.7	OCH_3, OCH_2	
1,1,3-Trimethoxypropane	16.7	OCH,	5.0 (OCH)

[1] *Units are in* cm^3*.molecule*$^{-1}$*.* s^{-1}*.* 10^{-12}.

In Table 6 a survey of the estimated reactivities of the respective structural parts in a glucose and a fructose unit is given. Also the simplest reference molecule, which bears the structural feature is indicated. The contribution of the 6-CH_2OH-group, both in starch and inulin, is estimated to be 4.10^{-12} cm^3.molecule^{-1}. s^{-1}, somewhat higher than the reactivity of ethanol.

The reactivity of each CHOH-group of the diol unit is estimated to be 9. 10^{-12} cm^3. $molecule^{-1}$. s^{-1}. In the fructan and glucose-unit the activation will be larger, due to the presence of the extra C-atoms (estimated is 11. $10^{-12}cm^3$.$molecule^{-1}$. s^{-1}). Hence the net reactivity of the glycolic moiety is estimated to be: 22. $10^{-12}cm^3$.$molecule^{-1}$. s^{-1}. The ether oxygen atoms will activate the moiety to a larger extent, possibly by a factor 3 or higher.

Table 6. Estimated reactivities of the structural features of glucose and fructose units as present in starch and inulin.

C-H bond under consideration	Reference compounds	k_{OH} of structural feature in fructose	k_{OH} of structural feature in glucose
1	glucose : 1,1- dimethoxyethane fructose: diethyl ether	5 (14)	5 (13)
2	glucose : ethylene glycol	0 (0)	11 (28)
3	glucose : ethylene glycol fructose: ethylene glycol	11 (31)	11 (28)
4	glucose : diisopropyl ether / 1,2 - dimethoxypropane fructose: ethylene glycol	11 (31)	5 (13)
5	glucose and fructose: diisopropyl ether/1,2-dimethoxypropane	5 (7)	5 (13)
6	glucose : ethanol fructose: ethanol	4 (7)	4 (7)

Between brackets the contribution in % is given to the total reactivity
Units are in cm^3. $molecule^{-1}$. s^{-1}. 10^{-12}. Between brackets the percentage of the contribution to the overall reaction is given.

The data given in Table 6 are estimates, but it can be concluded that a radical reaction predicts about 56% selectivity at the glycolic moieties of the glucose units of starch and 61% selectivity of the glycolic moiety of the fructose unit in inulin. If indeed the ether oxygen activates all adjacent C-atoms, a still higher selectivity is expected. The total reactivity of the diol group is then 66.$10^{-12}cm^3$.$molecule^{-1}$. s^{-1}, which means about 80%

selectivity. In Fig. 1 the reactivity of the respective structural features in an anhydroglucose and -fructose unit are shown.

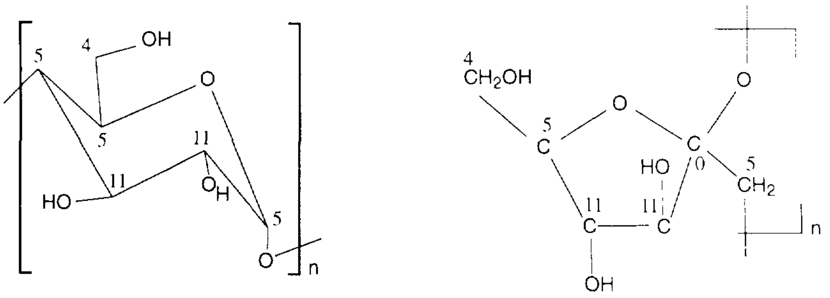

Fig. 1 The k_{OH} of the structural features of an anhydroglucose and anhydrofructose unit, respectively. Above the C-atoms the reactivity towards the OH-radical (in 10^{-12} cm^3. $molecule^{-1}$. s^{-1}) is given.

Obviously, more research directed to the elucidation of the mechanism is necessary. Ionization and possibly solvatation effects may probably further enhance the relative reactivity of the alcoholic functions. In this respect it is interesting to note that *Floor* [12] in the oxidation of starch observed more degradation products pH 7.0 than at pH 8.5.

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CHAPTER 5

THE CATALYTIC EFFECT OF BROMIDE IN THE HYPOCHLORITE OXIDATION OF LINEAR DEXTRINS AND INULIN

Summary

The effect of bromide in the hypochlorite oxidation of amylodextrins (short chain amylose) and inulin on the reaction rate was investigated. It was found both in the linear dextrins and inulin oxidation that the rate increases linearly with the sodium bromide concentration, which proves the catalytic effect of this substance. The origin of the catalysis is the rapid Br^-/OCl^- conversion. From the results the second-order rate constants of the reaction

carbohydrate + $HOBr/OBr^- \rightarrow$ products + HBr/Br^- were obtained.

For

linear dextrins: $k = 0.15\ M^{-1}.min^{-1}$ at 294 K and pH 9.0

and for

inulin : $k = 0.31\ M^{-1}.min^{-1}$ at 298 K and pH 9.0.
The activation energy for the oxidation of amylodextrins amounts to 67 $kJ.mole^{-1}$.

The highest rate was found at pH 8.25. The reaction rate is almost independent of pH in the region 8.5-9.5. Because of the simultaneous occurrence of bromine, Br_3^-, hypobromous acid and hypobromite in the pH region investigated, it is difficult to elucidate the mechanism with respect to both the behaviour of the oxidizing species and the oxidation of the substrate.

Introduction

The specific oxidation of the vicinal diol moieties of the glucose units in starch and cellulose and of the fructose units in inulin leads to polycarboxylates, which because of their calcium binding properties can be used as a substitute for (penta)sodium tripolyphosphate [1-7] or as a so-called co-builder in combination with zeolite NaA replacing polyacrylate or related compounds [5]. Because there is a need for biodegradable builders in detergent formulations there is growing interest in methods for the preparation of natural material-based polycarboxylates.

There are two suitable methods known for the glycolic oxidation of polysaccharides

- a two step method with $NaIO_4$ and $NaClO_2$ (process I)
- a one step conversion with NaOCl (process II).

The former procedure has the advantage that the products, obtained from starch have a sequestering capacity equal to that of phosphate or even exceeding it [5, 6]. However, due to the high molecular weight, possibly required to obtain a good sequestering capacity [6], it is expected that the biodegradability may be insufficient [3]. A further drawback is that for the production expensive chemicals are needed. The products which are obtained by the latter procedure have a lower molecular weight and lower calcium binding capacity than those obtained via route I. Because of the lower molecular weight the perspectives for biodegradability are better [3]. A second advantage is that the product will be cheaper since it is prepared in a single, simple step with a relatively inexpensive reagent. For these reasons the latter procedure is considered to be the most promising.

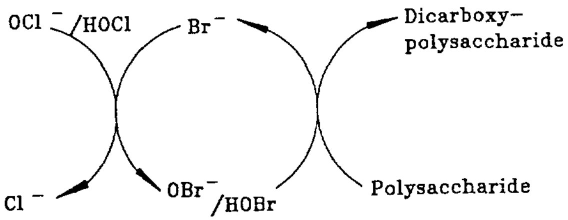
In the framework of our study concerning the hypochlorite oxidation of starch and inulin we felt that an improved procedure was needed and that perhaps the economic hypochlorite oxidation could be substantially improved. Several problems had to be solved.

Nieuwenhuizen et al. [5] state that the oxidation of starch with NaOCl yields coloured products. The use of a large excess of oxidant will make the dicarboxy-starch (too) expensive. If however less oxidant is used the reaction rate becomes too slow with the consequence that the oxidation is incomplete and formation of coloured products, probably during work-up is enhanced [8, 9].

From our studies [10, 11] it appeared that improvements indeed were possible. For instance a slow addition of the oxidant led to a higher yield and to products which were less coloured. Especially, the use of bromide as a catalyst was found to improve the whole process i.e. the yield was higher and somewhat better performing products were obtained. Other advantages are the higher reaction rate upon applying bromide-catalysis and the possibility to carry out the reaction at higher pH, which may be favourable to avoid the formation of coloured products. The effect of bromide on the reaction rate is to be attributed to the reaction

$$Br^- + OCl^- \rightarrow OBr^- + Cl^-$$

which occurs very fast [12].
A scheme for the bromide-catalyzed oxidation is given below.



The positive effect of bromide as a catalyst on the reaction rate and the perspective for a higher carboxylate content have already been reported by *Potze* and *Hiemstra* [13] in the partial oxidation of starch. *Floor* et al. [7] found in the complete oxidation of starch with sodium hypochlorite no effect at all. This may be attributed to the low amount of bromide, used by these authors in their experiment.
Experiments from others indicate that the use of hypobromite may be advantageous, both with respect to the rate and the product composition [14, 15].
As part of our study of the hypochlorite oxidation of polysaccharides we have investigated the kinetic parameters of the bromide-catalyzed reaction with the aim to prove the catalytic cycle. Substrates studied include a series of amylodextrins (1,4-α-glucans) and inulin (1,2- ß-fructans).

Experimental

Materials

Amylodextrins (linear dextrins) were prepared from waxy maize starch by enzymatic hydrolysis [16]. Gelatinized starch (8% suspension in water) was incubated at 55 °C and pH 5.0 during 24 hours with a pullulanase (Promozyme, NOVO). The dextrins, which precipitated after cooling, were collected by filtration, washed two times with methanol and dried in vacuo. The average degree of polymerization (DP) was determined by measurement of the reducing capacity [17] and the total carbohydrate content [18] and confirmed by HPLC-SEC [19, 20] and was found to be 25.

Inulin, isolated from chicory roots was obtained from Sigma chemicals; the average DP was 10.

Sodium hypochlorite of a commercial quality, was prepared by passing chlorine into a solution of sodium hydroxide in demineralized water. It contained about 100 g of Cl_2/l; for stabilization the solution contained a slight excess of NaOH (3 g/l).

Sodium bromide, acetic acid and the reagents for the titration of the sodium hypochlorite content of the reaction mixture (0.1 N titrisol, sodium thiosulfate, and potassium iodide) were obtained from Merck.

Methods

The experiments were carried out in a glass double-wall vessel with a volume of 150 ml. The reaction mixture was kept at a constant temperature and stirred magnetically.

The substrate was dissolved in 95 ml hot water. In the experiments with dextrins 1 g and in the experiments with inulin 2 g was used. In order to establish the dependence of the rate on the substrate concentration one experiment was carried out in which 5 g of inulin was used. The substrate solution was transferred to the reaction vessel. After cooling the mixture to the desired temperature 5 ml of NaOCl-solution and a known amount of sodium bromide were added. The pH was adjusted by the addition of 50% aqueous acetic acid.

In the first series of experiments, in which linear dextrins were used, the pH was kept at the desired value by means of a buffer solution (Na_2CO_3-$NaHCO_3$). In the second series, the experiments with inulin the pH was kept constant by adding 4 M NaOH-solution, controlled by a pH-stat (Radiometer). The consumption of hypochlorite was measured as a function of time. Samples (1 ml) were taken at time intervals of 5-10 minutes and analyzed for the hypochlorite content, adding the sample to an aqueous solution of KI-acetic acid and titrating with 0.1 N thiosulfate solution.

Results and discussion

Kinetics of the oxidation of linear dextrins

The rate of the oxidation of the linear dextrins with the sodium hypochlorite/bromide system was measured as a function of the sodium bromide concentration. The con-

centration of the substrate was 0.06 M. The molar ratio hypochlorite/glucose-units was approximately 1:1.24
It appeared that the decrease of the hypochlorite concentration as a function of time is linear, except for the first 5 minutes of the process, where a somewhat faster decrease is observed. A possible explanation for this behaviour is the absorption of Br_3^- which might be present at the pH examined (see Fig. 1 [21]). In the oxidation of starch with bromine similar phenomena have been observed [14]. In Fig. 2 the results of our experiments (rate vs. bromide concentration) are shown.

Because the reaction

$$Br^- + OCl^- \rightarrow OBr^- + Cl^-$$

and the dissociation/association reactions

$$HOBr \rightleftharpoons H^+ + OBr^-$$

are fast, the sum of the concentrations of HOBr and OBr^- may be considered to be constant[1] and equal to the initial bromide concentration.In a schematic way the oxidation can be formulated as follows:

$$\text{substrate} + OBr^- \xrightarrow{k'} \text{products} + Br^-$$

$$\text{substrate} + HOBr \xrightarrow{k''} \text{products} + HBr.$$

Hence $-dC_{Ox}/dt = k.C_{Ox}.C_{substrate}$ (with $k = k' + k''$ and Ox = oxidant). From this expression and the slope (dC_{Ox}/dt) follows that

$$k = 0.149\ M^{-1}.min^{-1} \text{ at } 294\text{ K and pH } 9.$$

Activation energy

The rate constant was measured as a function of temperature between 295 and 325 K. In all experiments the NaBr concentration was 1000 mg/l. The results are presented as an Arrhenius plot in Fig. 3. It follows that the activation energy is 67 $kJ.mole^{-1}$, which is close to the value for the hypochlorite oxidation given by *Schmorak* et al. (60 $kJ.mole^{-1}$,

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[1] The sum of the hypobromous acid and the sodium hypobromite concentration is designated as C_{Ox}.

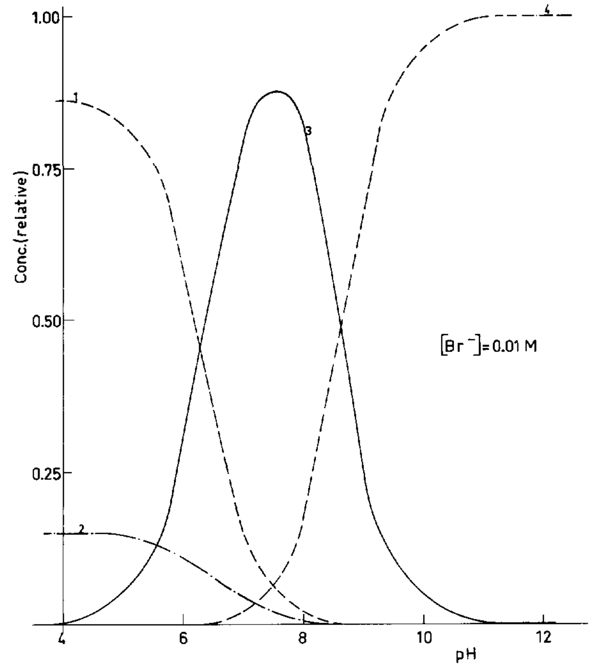

Fig. 1. Composition of a mixture containing bromine (1), Br_3^-(2), HOBr (3) and OBr^- (4) as a function of pH at 20 °C [21]. The initial bromide concentration is 0.01 M.

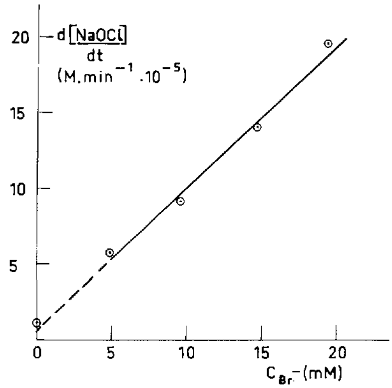

Fig. 2. The hypochlorous acid/hypochlorite consumption rate of the bromide-catalyzed oxidation of linear dextrins as a function of the bromide concentration. Substrate concentration 10 g /l (0.06 M), hypochlorite concentration 0.065 M; T = 21 °C, pH = 9.

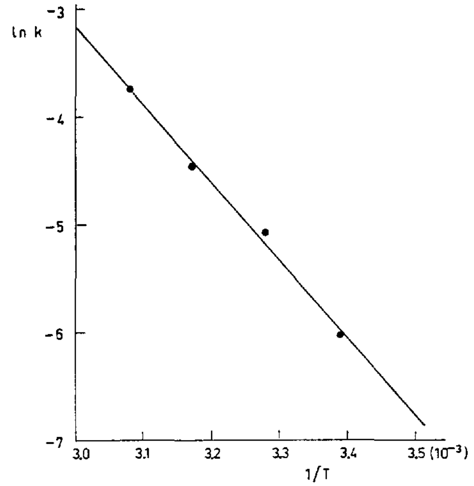

Fig. 3. Arrhenius plot of the oxidation of linear dextrins with the sodium hypochlorite-bromide system. $C_{amylodextrins}$ = *0.06 M,* C_{NaOCl} =*0.065 M,* C_{NaBr} = *1 g/l, pH = 9.*

[22]) and *Patel* et al. (67 kJ.mole^{-1}, [23, 24]) and to the values reported by *Ziderman* et al. for the oxidation of starch with bromine/HOBr (42-92 kcal/mole [14]).[1]

Effect of the sodium hypochlorite concentration on the reaction rate in the starch oxidation with the sodium hypochlorite-sodium bromide system

The rate of the bromide-catalyzed oxidation was determined at pH 9 for three sodium hypochlorite concentrations. The results are summarized in Table 3.

Table 3. Rate of the hypochlorite consumption in the bromide-catalyzed hypochlorite oxidation of linear dextrins.

Concentration OCl^-/HOCl (M)	Consumption rate ($M.s$-1.10^{-4})
0.16	3.4
0.20	4.5
0.40	4.1

$C_{amylodextrins}$= *0.06 M,* C_{NaBr} = *1000 mg/l, pH = 9, T = 295 K.*

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[1] *Ziderman* and *Bel-Achye* mention the latter range for the activation energy of the bromine/hypobromous acid/ hypobromite oxidation of starch. They refer to unpublished results of *Lewin* and *Schmorak* (ref. 3 in [14]).

It appears that the differences, probably to be attributed to experimental errors, are relatively small, which indicates that as expected the reaction rate does not depend on the hypochlorite concentration.

Experiments with inulin

The rate of the consumption of HOCl/OCl$^-$ in the bromide-catalyzed oxidation of inulin with sodium hypochlorite was determined at various bromide concentrations and over the pH range 8.25-9.5. The results are summarized in Table 4.

Table 4. Rate of the oxidant consumption in the oxidation of inulin with the sodium hypochlorite/bromide system at various pH.

Experiment	pH	$C_{Bromide}$ (mM)	dC/dt (M NaOCl.min^{-1}.10^{-4})
1	8.25	9.60	7.87
2	8.5	9.70	5.52
3	8.5	14.0	8.9
4	9.0	2.11	1.68
5	9.0	6.90	3.65
6	9.0	10.7	4.48
7	9.0	2.91	2.11
8	9.0	4.92	2.68
9	9.0	9.88	4.89
10	9.5	2.40	1.83
11	9.5	5.11	2.43
12	9.5	5.71	3.47
13	9.5	7.67	3.90
14	9.5	10.2	4.68

C_{inulin} = 0.12 M; T = 25 °C; C_{NaOCl}= 0.05-0.06 M.

In all experiments a fast initial consumption of hypochlorite was observed (Figures 4 - 6 show examples). If the consumption in the initial phase is omitted the hypochlorite consumption appears to be a linear function of time.
In Fig. 7 the relation between the rate of the consumption of reagent and C_{Br^-} is given. From the slope the second-order rate constant for the overall reaction

$$\text{inulin} + \text{HOBr/OBr}^- \xrightarrow{k_1} \text{products} + \text{HBr/Br}^-$$

can be calculated.

A survey of the rate constants, derived from these data, is given in Table 5.

The y-intercept (C_{NaBr} = 0) in the Figures represents the contribution of the hypochlorite consumption due to the " back-ground" reaction i.e. the hypochlorite oxidation of inulin

$$\text{inulin} + \text{HOCl/OCl}^- \xrightarrow{k_2} \text{products} + \text{HCl/Cl}^- .$$

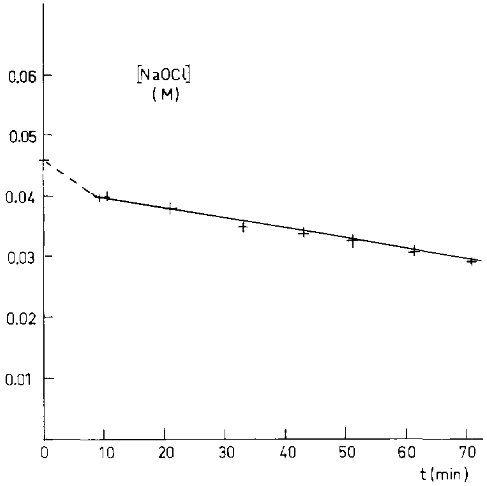

Fig. 4. Consumption of NaOCl in the oxidation of inulin with the sodium hypochlorite/bromide system at pH 8.5. C_{inulin} *= 0.12 M,* C_{HOCl/OCl^-} *= 0.06 M, T = 298 K,* $C_{bromide}$ *= 0.0021 M.*

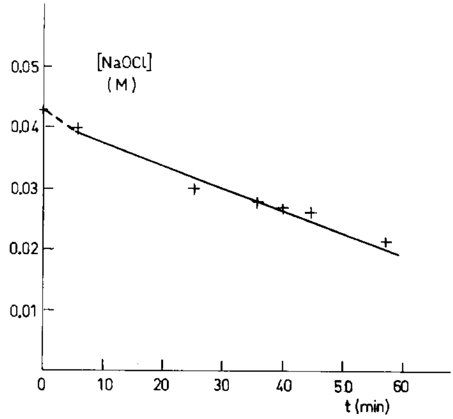

Fig. 5. Consumption of NaOCl in the oxidation of inulin with the sodium hypochlorite/bromide system at pH 9.0 and 298 K; C_{inulin} *= 0.12 M,* C_{HOCl/OCl^-} *= 0.06 M ;* $C_{bromide}$ *= 0.0069 M.*

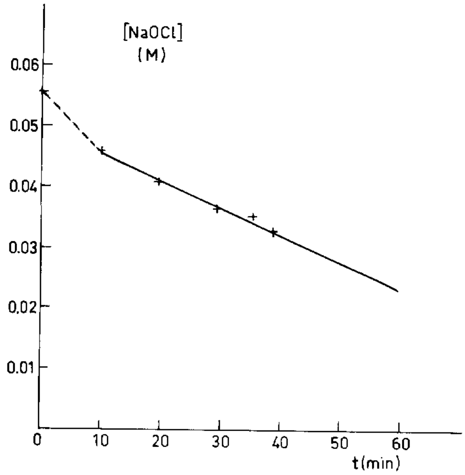

Fig. 6. Consumption of NaOCl in the oxidation of inulin with the sodium hypochlorite/bromide system at pH 9.5 and 298 K; $C_{bromide}$ *= 0.010 M;* C_{inulin} *=0.12 M.*

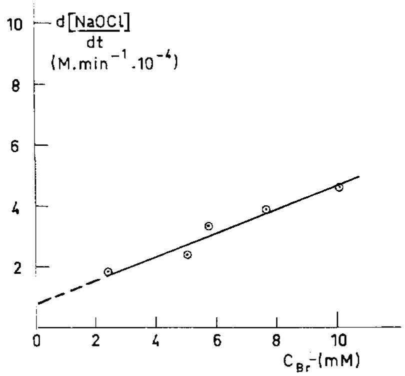

Fig. 7. Relation between NaOCl-consumption rate and concentration of sodium bromide in the hypochlorite/bromide oxidation of inulin; pH 9.0, T = 298 K, C_{inulin} = 0.12 M.

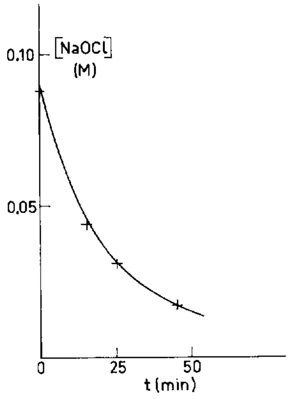

Fig. 8. Consumption of NaOCl in the oxidation of inulin at high concentration (0.3 M) with the sodium hypochlorite/bromide system at pH 9 and 298 K; $C_{bromide}$ = 0.09 M.

Table 5. Second-order rate constants of the reaction of inulin with the system $HOCl/OCl^-/Br^-$.

pH	T(K)	k_1 ($M^{-1}.min^{-1}$, OBr^-)	k_2 ($M^{-1}.min^{-1}$, OCl^-)
9.0	300	0.28	0.014
9.0	298	0.40	0.011
9.5	298	0.32	0.011

In literature no rate constants at these pH values are mentioned. For a comparable system, but at pH 8 and 303 K *Ziderman* and *Bel-Achye* [14] report for the oxidation of starch the pseudo-first-order rate constant (excess starch)

$k = 0.0131\ min^{-1}$at $C_{starch} = 5.4\ g.l^{-1}$.
From these values the second-order rate constant can be calculated $k_2 = 0.39\ M^{-1}.\ min^{-1}$.

Taking into account the temperature at which these measurements have been carried out (303 K) and the activation energy for the reaction with linear dextrins as substrate, 67 $kJ.mol^{-1}$ one finds at 300 K and at 298 K 0.31 $M^{-1}.\ min^{-1}$ and 0.25 $M^{-1}.\ min^{-1}$, respectively. As the rate constant does not seem to vary to a large extent with pH there seems to be a reasonable agreement. Also the rate constant of the dextrin-hypobromous acid/hypobromite oxidation at 295 K agrees rather well:

$k_2 = 0.15\ M^{-1}.\ min^{-1}$ at 295 K, which gives at 300 K 0.26 $M^{-1}.min^{-1}$.

From the measurements of *Schmorak* et al. [22] and *Patel* et al. [23, 24] a few rate constants for the hypochlorite oxidation of starch can be derived

$k = 0.005\ M^{-1}.\ min^{-1}$ at pH 9 and 300 K [22];

$k = 0.013\ M^{-1}.\ min^{-1}$ at pH 8.5 and 300 K and $k = 0.007\ M^{-1}.min^{-1}$ at pH 10 and 300 K [22, 23]. These rate constants have been measured with starch suspended in water; the authors found that in a homogeneous system the reaction proceeds about 50% faster. Accounting for this it is to be concluded that the rate constants as determined by us for inulin are in reasonable agreement with those mentioned above (for starch).
From the results of an experiment with high inulin concentration follows that the reaction rate increases with increasing substrate concentration. Due to the unknown contribution of the absorption in the initial phase of the reaction a rate constant cannot be measured. Based on the consumption between 15 and 25 minutes the rate constant

is found to be 0.4 $M^{-1}.min^{-1}$ in reasonable agreement with the rate constant mentioned above. This indicates a first-order behaviour with respect to the substrate.

Based on these data it can be shown that *Floor* et al. [7] could not observe any catalytic effect of bromide in their experiments. They oxidized starch (C_{starch} = 0.25 M) with NaOCl (C_{NaOCl} = 0.75M) at pH 8.5 and 293 K. Based on the rate constants measured by *Schmorak* et al. [22] the contribution, due to the presence of sodium bromide is given by $k_2 \cdot C_{starch} \cdot C_{NaBr}$. Then the contribution amounts to approximately 6%.

Mechanism

The system bromine/hypobromous acid/hypobromite is reactive over a wide pH range. Therefore both HOBr and OBr^- appear to be reactive towards carbohydrates. From the experiments of *Ziderman* and *Bel-Achye* [14], *Torneport* et al. [25] and *Salomonsson* et al. [26] it can be concluded that also bromine, mainly present below pH 8 (Fig. 1) is reactive. It may be noted that on the analogy of the hypochlorous acid/hypochlorite reaction which has been postulated to proceed through radicals, the occurrence of such a mechanism cannot be excluded. However, in that case a larger pH dependence should be observed.

A final but important remark concerns the value of the rate constants. In all oxidations with $HOCl/OCl^-$ and $HOBr/OBr^-$ the production of carboxylate groups starts nearly immediately after the addition of the oxidant. This means that the primary products are very reactive and that immediately after the initial oxidation step, leading to the consumption of 1 molecule of oxidant 2 *extra* oxidant molecules per glucan/fructan unit are consumed. This means that the rate constants as presented in the literature and also in this paper are approximately three times too high, when one focusses on the first step.

Conclusions

Summarizing it can be stated that bromide indeed has a catalytic effect on the rate of the sodium hypochlorite oxidation of carbohydrates:

- the reaction rate increases proportionally with the bromide concentration
- provided sufficient catalyst is present, the rate is independent of the sodium hypochlorite concentration.

Some other conclusions are:

- the reaction rate is highest between pH 6-11 (experiments in literature included); in the pH region 9 - 10, the dependence of the rate is only slight, suggesting that all oxidizing species, Br_2, BrO^- and HOBr, contribute to the reaction to a comparable extent.

- no conclusive evidence can be drawn regarding the mechanisms of the reaction
- the reaction seems to be first-order both in the hypobromous acid/hypobromite and in the carbohydrate concentration
- the temperature dependence follows the Arrhenius expression; the activation energy is 67 $kJ.mol^{-1}$.

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CHAPTER 6

THE RELATION BETWEEN CALCIUM SEQUESTERING CAPACITY AND OXIDATION DEGREE OF DICARBOXY-STARCH AND DICARBOXY-INULIN

Summary

An experimental study has been carried out with the objective to establish the relation between the calcium sequestering capacity (SC) of dicarboxy-starch and of dicarboxy-inulin, and the oxidation degree of these products. It was established that oxidized starch exhibits a non-linear behaviour in this respect i.e. at a low degree of oxidation the SC is low. A sharp increase is observed when the degree of oxidation increases from 40 to 60%. Further conversion only leads to a modest increase. Contrary to this the sequestering capacity of dicarboxy-inulin increases linearly with the degree of oxidation. The difference in behaviour of these materials has to be attributed to the fact that upon starch oxidation the favourable oxydiacetate structure is obtained only after substantial conversion, whereas in inulin this structure is obtained immediately and is present in each oxidized fructose unit.

Introduction

Polysaccharides of the glucan-type (starch, cellulose) yield after oxidation of the vicinal diol group of the glucose-units polycarboxylates which exhibit calcium ion sequestering properties and seem to be suitable for use as (co-)builders in laundry detergent formulations [1-9]. Two methods have been investigated extensively and have shown to be suitable for an efficient preparation procedure:

1. a two step process consisting of consecutive oxidation with $NaIO_4$and $NaClO_2/H_2O_2$
2. a one step reaction with NaOCl.

Nieuwenhuizen et al. [5] and *Floor* et al. [8] have shown that the two-step process yields the best performing products. This is attributed to the fact that the high molecular weight of starch and cellulose is retained during the oxidation, whereas with sodium hypochlorite some depolymerization occurs. There are several reasons to doubt whether the molecular weight is the most important factor determining the calcium binding. Evidence that the oxidation degree is another important parameter can in fact be deduced from the results of *Floor* et al. [7, 8] by examining the sequestering capacities reported for the various products.

Thus a product which was obtained by hypochlorite oxidation of starch had a sequestering capacity of 1.04 mmole Ca/g and a carboxylate content of 5.43 mmole COONa/g)[1]. A second oxidation of this material yielded a product from which the carboxylate content was increased with 25% to 6.77 mmole COONa/g; the sequestering capacity however, increased sharply with 60% to 1.77 mmole Ca/g. It is remarkable that the average degree of polymerization (DP) was much lower than that of the first product.

In another series of experiments [8] materials were obtained by partial oxidation of dialdehyde starch with sodium chlorite/hydrogen peroxide. It appeared that a relatively small increase in carboxylate content leads to a large increase in sequestering capacity. At our laboratory we observed similar phenomena in the hypochlorite oxidation of starch. It was also established that the behaviour of the fructan inulin was quite different. The sequestering capacity seemed to be linearly dependent on the oxidation degree. In view of these (preliminary) results we have studied the partial oxidation of starch and inulin in more detail, allowing to compare these carbohydrates with respect to their respective structure after oxidation. Especially inulin had our attention, because the ODA-structure, being favourable for calcium complexation [10, 11] is readily obtained upon oxidation.

It may be advantageous to use partially oxidized products. If they have satisfying properties with respect to calcium and magnesium binding, they may be used as a co-builder. The biodegradability of partially oxidized polycarboxylates may be better since in the remaining intact sugar units microorganisms might find an ensemble of

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[1] The carboxylate content of a completely oxidized product is 8.47 mmol (as COONa)/g

recognition[1]. It seems therefore useful to study the relationship between oxidation degree and sequestering capacity.

Experimental

Materials

The following chemicals were used:

- sodium hypochlorite was of a commercial quality and prepared by passing chlorine into a solution of sodium hydroxide in demineralized water. The concentration was about 100 g Cl_2/l
- sodium hydroxide (Merck p.a.) was used as a 5 M solution
- sodium bromide and acetic acid were of p.a. quality, supplied by Merck
- (wheat) starch was a gift from Latenstein (Nijmegen, the Netherlands)
- inulin with DP = 10, isolated from chicory roots, was a gift from Suiker Unie (Roosendaal, the Netherlands)
- inulin with DP = 30, isolated from dahlia tubers, was obtained from Sigma Chemicals.

Methods

The oxidations were carried out in a 150 ml reaction vessel. Provisions were present for pH measurement and NaOH-addition. The pH was kept constant by addition of sodium hydroxide solution, which was controlled by a pH-stat (Radiometer).
For the measurement of the sequestering capacity[2] a calcium ion selective electrode (F 2002, Radiometer) was used, in combination with a calomel electrode (K 401, Radiometer).

a. oxidation of inulin

In the reaction vessel a solution of 4.85 g chicory inulin (27 mmole anhydrofructose and 3 mmole glucose-units) in 25 ml water was brought. To this mixture 200 mg of

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[1] Recently *Matsumura* et al. (1991) described in a Japanese paper that the biodegradability of oxidized starch decreases with increasing number of oxidized glucose units.

[2] The sequestering capacity is defined as the amount of mmole Ca(II) that will be bound by 1 g of the sequestering agent at pH between 10 and 10.5 until the residual concentration of Ca(II) is 10^{-5}M.

NaBr and 75 ml of a NaOCl solution (theoretical amount) were added. The reaction was carried out at 25 °C until about 60% NaOCl was consumed and the reaction rate declined; the temperature was subsequently raised to about 40 °C. During the reaction the pH was kept constant by addition of NaOH-solution, controlled by a pH stat; the-NaOH consumption was measured as a function of time. This parameter correlates closely with the consumption of hypochlorite, so that from the NaOH consumption the degree of oxidation may be derived (see also *Floor* et al. [7] and *Epstein* and *Lewin* [12]). During the oxidation the sequestering capacity of the reaction mixture was measured as a function of the conversion degree. Samples were added to 100 ml water containing 1.10^{-3} M Ca(II) and 5.10^{-3} M NaCl. From interpolation of the titration curve (see Fig. 2) the amount for lowering the Ca(II) concentration to 10^{-5}M was determined.

b. oxidation of starch

To 5.0 g of starch, suspended in 25 ml water, a known volume of a solution of sodium hypochlorite was added, followed by 250 mg of NaBr. After adjustment of the pH by addition of a small amount of aqueous acetic acid solution, the reaction was allowed to proceed at 25 °C until the reaction rate declined, which was the case after approximately 60% of the hypochlorite was consumed. Upon heating the mixture at 45 °C the reaction was completed. The sequestering capacity of the solution as a function of the oxidation degree was measured as described above.

Results and discussion

Consumption of sodium hypochlorite vs. acid production

Both from the experiments with starch and with inulin we found that the consumption of 3 moles of NaOCl resulted in the production of approximately 2 moles of polycarboxylate groups as shown in Fig. 1. This is in harmony with the reaction equation. It can be concluded that in agreement with the results described in literature [7, 11] the degree to which the reaction has proceeded, can be measured via measurement of the NaOH-consumption.

Oxidation of inulin

The oxidation of chicory inulin while monitoring the sequestering capacity of the reaction mixture was carried out at pH 9.0, 9.5 and 10.0.
An example of a Ca-titration curve of an isolated product is given in Fig. 2. The result of a representative measurement is given in Fig. 3.

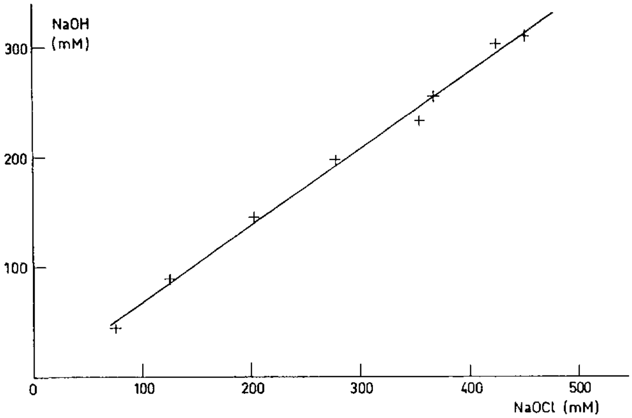


Fig. 1. NaOH-consumption vs. NaOCl-consumption in the oxidation of inulin.

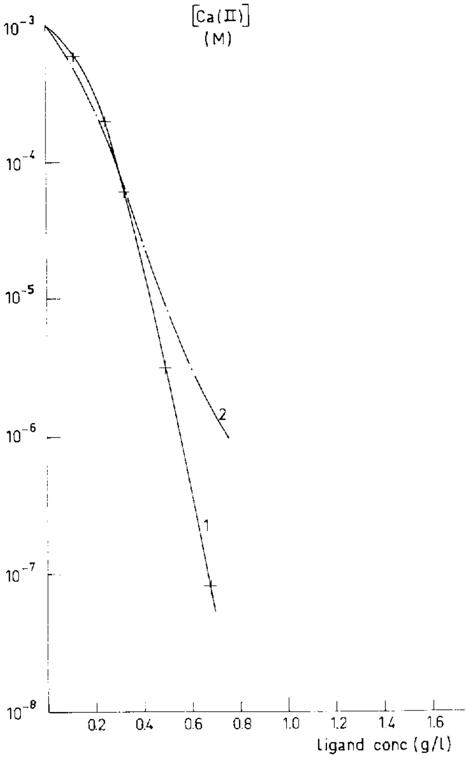


Fig. 2. Titration curve of oxidized inulin. Dicarboxy-inulin as disodium salt (line 1) or of samples of a reaction mixture (90% yield assumed) were added to a solution containing 10^{-3} M Ca(II). The resulting $C_{Ca(II)}$ was measured with an ion selective electrode.

For all pH values investigated a linear relationship is observed: an increase in degree of oxidation leads to a proportional increase in the calcium sequestering capacity.
In Fig. 4 the results are given for a similar experiment conducted with inulin from dahlia tubers, carried out at pH 9.5.

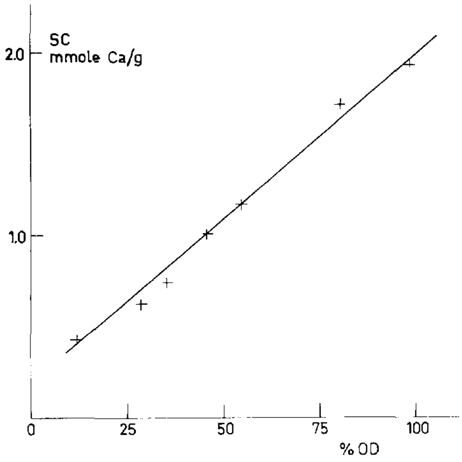


Fig. 3. Relation between sequestering capacity and oxidation degree of inulin oxidized at pH 9.5.

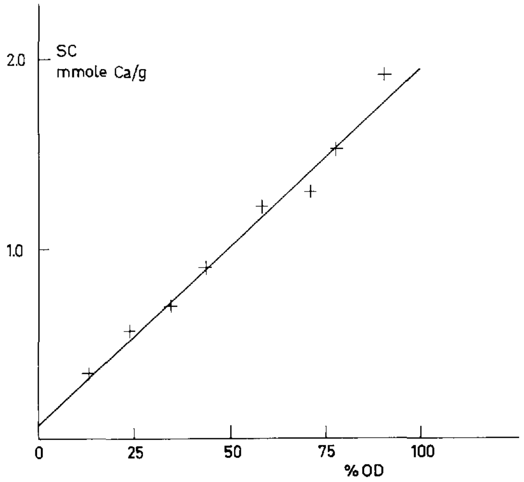
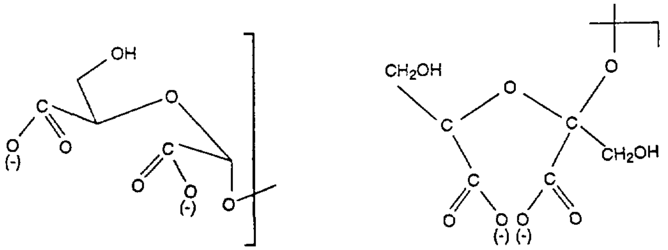


Fig. 4. Relation between sequestering capacity and oxidation degree of dahlia inulin oxidized at pH 9.5.

The slope (SC/OD) in the experiment with dahlia inulin as substrate is somewhat higher than in that with chicory inulin: 0.74 and 0.62 mmole Ca are found to be bound per mmole oxidized fructan unit, respectively. The difference may be due to the higher molecular weight of dahlia-inulin.

However, another explanation may be given for the difference. The oxidation of the terminal glucose unit will require more reagent (5 mole NaOCl per unit) than the oxidation of a fructose units (3 mole of NaOCl per unit).[1] In the next figure the expected structures are shown.



Dahlia inulin, containing more fructose units than chicory inulin will be more effectively oxidized than chicory inulin and hence will afford a somewhat better performing product. Based on this assumption dahlia inulin will have a sequestering capacity which is 7-10% higher than that of chicory inulin.

Oxidation of starch

It appeared from our experiments that the method developed for the determination of the relation sequestering capacity-oxidation degree of inulin is less suitable for starch (probably owing to the large amount of NaCl, which influences the complexation behaviour in a negative way). By carrying out the experiments with 25, 50, 75 and 100% of the stoichiometric amounts, respectively, satisfactory results could be obtained. A typical result is presented in Fig. 5.

As mentioned above the different behaviour with respect to the relation sequestering capacity and oxidation degree in the hypochlorite oxidation of starch has been noted by Floor [6]. In Fig. 5 the results of *Floor* et al. [7] in the $NaIO_4/NaClO_2$ oxidation with respect to the sequestering capacity and the degree of oxidation of starch are presented. *Nieuwenhuizen* et al. [5] have indicated that upon complete oxidation of starch the ODA-structure will be formed from two adjacent oxidized glucose units.

When the oxidation of the glucose units in starch occurs at random it will be expected that especially in the initial phase only moieties with the structure depicted in Fig. 6a will be formed. Thus in the initial phase the sequestering capacity only depends on the

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[1] Oxidation of the CH_2OH-group requires 2 moles of oxidant.

number of single oxidized glucose units[1] (Fig. 6a). When the reaction proceeds the number of adjacent oxidized units will sharply increase (Fig. 6b), and herewith the sequestering capacity. A more detailed study about this subject and directed to structural and conformational effects is required to obtain more insight into these phenomena.

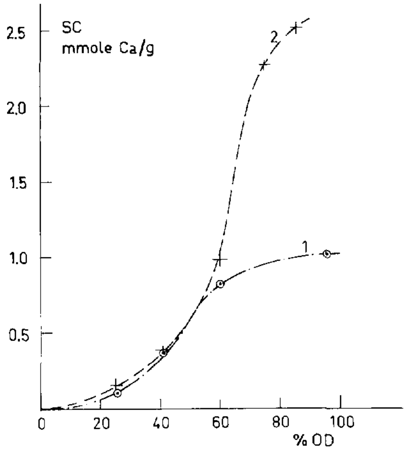

Fig. 5. The sequestering capacity of partially oxidized starch; line 2 represents Floor's results ($NaIO_4$/ $NaClO_2$- H_2O_2 oxidation); line 1 represents the results of the NaOCl/NaBr oxidation.

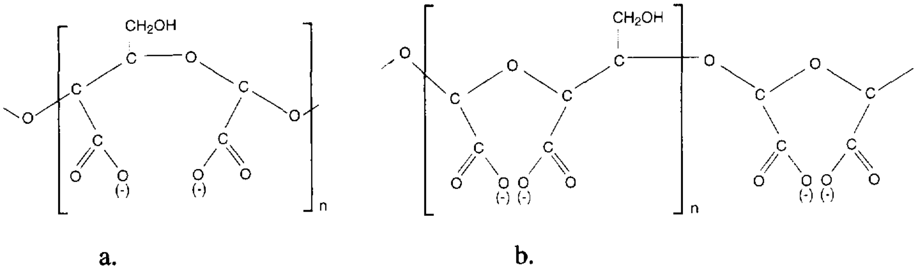

Fig. 6. Structure of glycol oxidized glucose units in an 1,4-α-glucan, see text.

The idea that the number of carboxylate groups is the determining factor for the sequestering capacity may also explain the difference in sequestering capacity of the products prepared via the hypochlorite and via the $NaIO_4$/$NaClO_2$- H_2O_2 method. The oxidation degree of hypochlorite oxidized starch is based on determination of the number

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[1] The SC of this unit is unknown, but based on these experiments is expected to be low.

of carboxylic acid groups. In chapter 2 of this thesis we have mentioned that part of the carboxylic acid groups (10%) probably is present as lactone, and is liberated in alkaline medium at higher temperature).

We consider it to be likely that these "hidden" carboxylic acid groups are present in the form of lactones. This means that the oxidation degree with respect to the carboxylate content has to be corrected: a small part of the carboxylate groups is present without a completely oxidized partner and is not expected to be involved in the strong calcium coordination.

Conclusions

The behaviour of partially oxidized starch and inulin with respect to the binding of calcium ions appears to be quite different. The sequestering capacity of oxidized starch is at low oxidation degree correspondingly low but when > 40% of the glucose units is converted a further oxidation leads to a sharp increase in SC until approximately 65% oxidation is reached. From this point further oxidation results only in a slightly better performing product. The initial effect can be understood by considering the fact that in α-1,4-glucans two neighbouring oxidized glucose units are required to provide a strong calcium binding (ODA)-site. In the case of inulin each oxidized fructose unit provides such an ODA-site directly.

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CHAPTER 7

CONFORMATIONAL STUDY ON THE COORDINATION OF CALCIUM IONS BY DICARBOXY-INULIN

Summary

Various aspects of the calcium coordination of dicarboxy-inulin (DCI) have been investigated with the aim to propose a conformation which explains the calcium binding strength of this material. From measurements of the optical rotation and the complex constant as a function of the DCI-Ca ratio, evidence is obtained that two kind of complexes exist. The first one is formed at high Ca-DCI ratio, leading to a complex in which one calcium ion is bound by one glycol-oxidized fructose unit. The second complex is found at low Ca-DCI ratio: one calcium ion is bound by two dicarboxy-fructose units. These conclusions could be confirmed by NMR spectroscopy measurements, carried out with the closely to Ca(II) related Dy(III) and Gd(III). It could be deduced that seven or eight oxygen atoms of DCI may be involved in the calcium coordination. The data available do not allow a definite proposal for the conformation of the DCI-Ca(II) complex.

Introduction

The complexation of calcium ions by organic compounds has been the subject of numerous studies. Especially the research directed to the replacement of sodium tripolyphosphate (STP) in laundry detergent formulations has been an important goal. When being present in too high concentration levels STP causes eutrophication of lakes, and even seas.

Numerous organic compounds have been synthesized and investigated with respect to their calcium binding properties [1-3]. Most of the substances investigated are compounds containing carboxylate and hydroxyl groups and ether linkages.

Two important classes of compounds to be considered are the synthetic polycarboxylates (polyacrylate and copolymers of maleic and acrylic acid, presently being used in substantial quantities as a co-builder together with zeolite NaA) and the semi-synthetic oxidized polysaccharides [4-13], such as the glucans cellulose and starch and its fractions, amylopectin and amylose, and cyclo- and maltodextrins. Upon oxidative cleavage of the diol group of these polysaccharides materials with excellent calcium binding properties are obtained. From our investigations it appeared that an alternative for these compounds may be oxidized inulin, which despite its low-molecular weight is a very good sequestering agent [14]. This property is attributed to the multiple occurrence of the oxydiacetic acid (ODA) structure [15]. In Fig. 1 this structure and the structure of oxidized inulin are depicted.

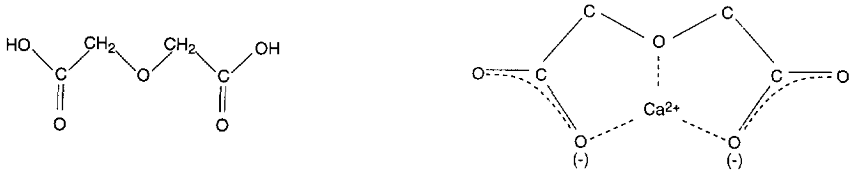

Fig. 1. Structure of oxydiacetic acid (ODA) and of oxidized inulin.

Many mono-, di-, oligo- and polysaccharides coordinate calcium ions. For instance, the industrial glucose/fructose separation over a Ca-ion exchange resin, or a Ca-loaded zeolite is based on differences in Ca-coordination strength of glucose and fructose. Well-known is also the binding effects of calcium ions with the natural 6-COOH polysaccharides pectin and alginate [16]. In the crystalline calcium salts of mono- and disaccharides usually 5 - 10 donor sites are involved [18]. If insufficient sites are available water molecules will participate. Such a situation is apparently met in the coordination of calcium with oxydiacetate [11, 16]. This molecule adopts a W-shaped form in which calcium is coordinated in a tridentate fashion via the carboxylic acid groups and the ether oxygen. The complex constant of this compound is relatively low (log K_{Ca}= 3.8; *cf.* the constants for STP and nitrilotriacetic acid (NTA) are log K_{Ca} = 6.0 and log K_{Ca} = 6.6, respectively). Apparently the number of binding sites (4 in STP and NTA) is an important factor.

The calcium binding properties of oxidized starch, cyclodextrins and cellulose are attributed to the presence of ODA units, which are obtained upon oxidation of two adjacent glucose units, see Fig. 2.

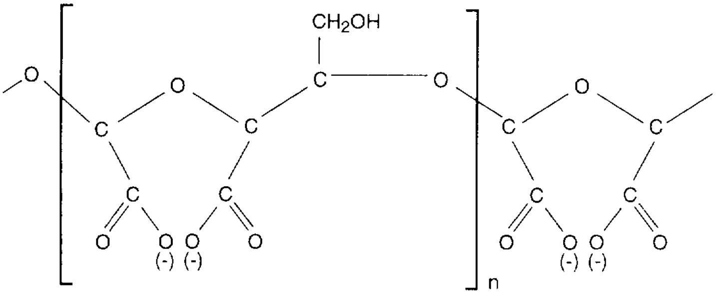

Fig. 2. ODA structure in oxidized starch.

Nieuwenhuizen et al. [7] established that in the coordination of Ca(II) with oxidized starch at least 7 non-water oxygen atoms are involved. Because only four active sites occur in one oxidized glucose-moiety the authors concluded that a conformation may be obtained, in which one calcium ion is coordinated between two oxidized glucose moieties. These authors proposed a helical conformation.

Floor et al. [12] directed their study especially to the coordination of calcium and lanthanide ions with oxidized ß-cyclodextrin. From their investigations it appeared also that in the complexation at least 7 oxygen atoms may be involved. They proposed on the basis of the behaviour of lanthanide[1] ions that two such ions are trapped within the cavity of a dicarboxy-cyclodextrin molecule[2].

Although the general structural features of 3,4-dicarboxy-inulin are similar to those of 2,3-dicarboxy-starch some differences may be noted:

- the degree of polymerization of inulin (10 when chicory is the source) is much lower than that of starch (>1000)

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[1] The complexes of lanthanide ions and those of Ca(II) are often isostructural.

[2] It is important to note that upon glycolic oxidation the original properties of cyclodextrins are lost i.e. the hydrophobic inner site of this molecule does not exist anymore. Instead a hydrophilic core is created.

- upon oxidation the ODA-structure, which is favourable for Ca(II) coordination, is obtained immediately for each anhydrofructose unit.

Despite the lower average molecular weight of inulin, the calcium sequestering capacity of oxidized inulin (2.3 mmole Ca/g) is comparable to that of dicarboxy-starch (2.5 mmole Ca/g).

It is tempting to attribute this to the formation of the ODA-structure. However, as mentioned above, the complex constant of this moiety is rather low and it is expected that more oxygen atoms of dicarboxy-inulin are involved in the complexation with metal ions. To elucidate this point an experimental programme was carried out including NMR spectroscopic techniques and optical rotation measurements.

Experimental

Materials

Inulin, isolated from chicory root, was obtained from Sigma chemicals; the average degree of polymerization (DP) of these samples was determined by NMR spectroscopy, using the characteristic signals of the protons of glucose and fructose, and amounted to approximately 10.
Sodium hypochlorite solutions were of commercial quality and prepared by passing chlorine gas into an aqueous solution of sodium hydroxide. The solution contained about 100 g/l Cl_2 and was stabilized with a slight amount of NaOH (0.3%).
Sodium hydroxide solutions were prepared from NaOH (p.a. quality Merck). Methanol, calcium chloride and magnesium sulfate were obtained from Merck; ethanol (96%) was obtained from Gist-brocades.

Methods

a. oxidation

The oxidation of inulin was carried out in a 150 ml double-wall vessel equipped with inlets for NaOH-dosage and addition of sodium hypochlorite solution and a pH glass electrode. To a solution of 4.85 g (27 mmole anhydrofructose units and 3 mmole 1-O-substituted glucose units) of inulin and 250 mg of sodium bromide in 25 ml of water a few ml of NaOCl solution were added. After an initial sharp rise of the pH (11-11.5) a fast decline was observed due to acid formation. The stoichiometric amount of NaOCl (about 75 ml, 90 mmole) was added in the course of 6-8 hrs. Throughout the experiment the pH was kept at 10 by addition of NaOH-solution, which was controlled by a pH stat. After 6 hours about 60% of the oxidant was consumed; the temperature was gradually raised to 45-50 °C. After about 24 hours of reaction time > 95% of the amount of sodium hypochlorite was consumed. The reaction mixture was concentrated under reduced pressure to a volume of about 50 ml. The solution was poured into 150 ml well-stirred 96% ethanol. After standing for one day the liquid was decanted from the oily or solid residue. This was dissolved in 50 ml demineralized water and poured into 175 ml absolute methanol. In order to avoid oil formation this procedure was carried out very carefully i.e. the solution was slowly added in small amounts to the well-stirred methanol. Usually a white solid was obtained, which was collected by filtration and dried in vacuo at 50 °C. An oil formed can be converted into solid material by grounding the oil with absolute methanol. The percentage dicarboxy-inulin as disodium salt of the material, containing sodium chloride and water, was determined by converting the material into the acid form by ion exchange and freeze-drying, herewith removing the volatile hydrochloric acid. The percentage dicarboxy-inulin was calculated with M = 236 for the disodium salt and M = 192 for the acid form. The percentage of the carboxylate groups in the material was determined by titration of the acid with 0.2 M NaOH-solution. Evidence was obtained that a small part of carboxylate groups (8-10%) may be present as lactone (see chapter 3 of this thesis for more details).

b. determination of the sequestering capacity and the intrinsic complex constant (K_{int}).

The calcium sequestering capacity (SC) was determined by measurement of the calcium ion concentration with a Ca-ion selective electrode. The procedure was as follows. To 100 ml of an aqueous solution containing 10^{-3} M Ca(II) and 5.10^{-3} M NaCl known amounts of dicarboxy-inulin as disodium salt were added. The pH was, if necessary adjusted to 10-10.3. After 2 minutes of stirring the resulting concentration Ca(II) was measured. For the calibration of the ion-selective electrode aqueous solutions of 10^{-2}, 10^{-3}, 10^{-4}, 10^{-5} and 10^{-6} M $CaCl_2$, each containing 5.10^{-3} M NaCl, were used. The calibration curve (log U vs. concentration Ca(II)) was linear between 10^{-2}-10^{-5} M; below this concentration the sensitivity of the electrode decreases in accordance with the specifications of the supplier, but again a linear relationship was found to exist and reproducible measurements could be carried out to C $>10^{-8}$ M Ca(II).
The calcium sequestering capacity is defined as the number of mmole Ca(II) that will be bound by one gram sequestering agent at pH 10-10.5 until the concentration of non-bound Ca(II) is 10^{-5} M. This value is considered to be the upper limit in the washing process for preventing incrustation.
Another approach of characterizing the material with respect to calcium binding is measuring the complex constant [12].

$$K = [\text{Complex}]/[\text{Ca(II)}].[\text{Ligand}]$$

For polymeric compounds containing many, identical coordinating sites the method of Tanford [17] has to be applied. For the characterization of dicarboxy-starch this method has been proven to be a useful approach. The complex constant of a calcium coordinating polymer is a function of the number of occupied sites with calcium ions.

$$K_{int}\, e^{cZ} = [Z]/[Ca(II)][1-Z]$$

where Z is the fraction of the occupied sites and c is a constant.
An intrinsic complex constant K_{int} is defined at Z = 0. It is questionable whether this approach may be applied for dicarboxy-inulin because inulin is a relatively small polymer with an average DP = 10. However, it is clear that the extent to which calcium is bound, will influence the coordinating behaviour of the remaining, non-bound sites of the molecule. An effective complex constant K at Z = 0.1 may be defined as well. Therefore measurement of the complex constant in relation to the amount of Ca(II) may provide useful information.

c. Job's plot

Solutions of dicarboxy-inulin (as disodium salt) and calcium chloride (both 5.10^{-3}M) were mixed at different ratios and the resulting Ca(II) concentration was measured, as described above. From the results the concentration of the calcium complex can be derived.

d. NMR spectroscopy

^{13}C NMR (100.6 MHz) and ^{17}O NMR (54.2 MHz) spectra were recorded on a Varian VXR-400 S spectrometer with D_2O as the solvent. The ^{13}C chemical shifts are reported with respect to the methyl signal of t-butanol as internal standard at 31.2 ppm.

e. Optical rotation

Optical rotation measurements were carried out with a Polarimeter (Perkin-Elmer 241). Solutions of DCI were mixed with various amounts of $CaCl_2$-solution. The final concentration of DCI was 5mM. The optical rotation of the resulting solution was measured at 25 °C in a 1 dm tube.

Results and discussion

Job's plot

The results of the measurements for Job's plot are presented in Fig. 3. It appears that under these conditions (a relatively high concentration calcium at the maximum) one calcium ion is bound by two COO^- groups i.e. the optimum of the complex concentration is found at $R_{[Ca0]/[Ca0]+[DCI]} = 0.5$. In other measurements, carried out with other samples this ratio was found to be 0.40-0.55. In addition we carried out some measurements with magnesium sulfate[1], from which it can be concluded that under these conditions similarly one ion is coordinated with two carboxylate groups. It has to be emphasized that at lower ion concentration the complex stoichiometry may differ. This aspect will be discussed below in more detail.

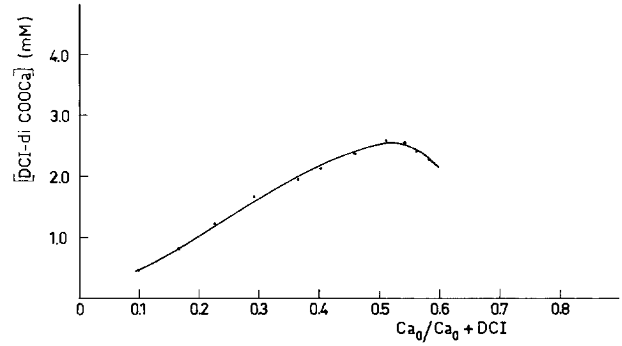

Fig. 3. Job's plot for dicarboxy-inulin.

Optical rotation

In Fig. 4 an example of the results of the measurements of the optical rotation as a function of the calcium concentration is given.

Upon addition of Ca(II) a linear decrease of the rotation takes place until the Ca(II) /ligand ratio (ρ) = 0.31-0.33 is reached[2]. At a higher calcium concentration no further change occurs (because the carboxylate content is about 65% this value has be to corrected to ρ = 0.46-0.49). This suggests that going from a low to a higher calcium concentration the composition and conformation of the complex changes, until a complex stoichiometry of one Ca(II) to two carboxylate groups is reached and no further change occurs.

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[1] The concentration of magnesium ions can be measured with a Ca-ion selective electrode, if no calcium ions are present.

[2] ρ is based on the assumption that the product used is fully oxidized with M = 236. At ρ = 1 one Ca(II) is coordinated by one dicarboxy unit.

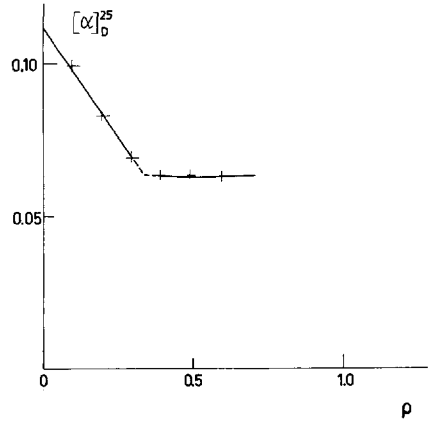

Fig. 4. Optical rotation of complexes of DCI and Ca(II).

Tanford's plot

A few examples of a Tanford plot are presented in Fig. 5. The complex constant (approximately log K = 4.0 between Z = 0.6 and Z = 0.9) increases slowly until Z = 0.5 and then increases more sharply. Typical values for log K_{int} are 9-10.5, which implies that at a high dicarboxy-inulin calcium ratio strong complexes are formed.

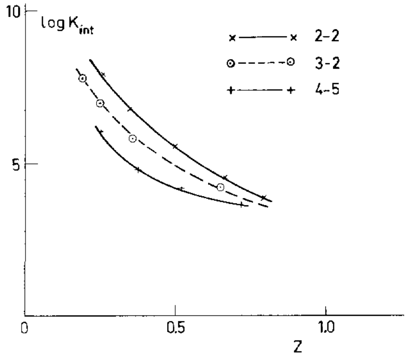

Fig. 5. Tanford's plot for some samples dicarboxy-inulin (see Chapter 3, Table 5).

In addition to the results of the optical rotation and of Job's plot these measurements suggest that at a relatively high concentration of calcium one ion is bound by one monomeric unit i.e. by two carboxylate groups and the ether oxygen atom. This is also reflected by the value of the complex constant (log K = 4.5-5.5 at Z = 0.5) which is slightly higher than the complex constant of oxydiacetate (log K = 3.8). Upon decreasing the Ca(II) concentration, apparently more groups are involved in the binding of this ion, as follows from the sharply increasing complex constant. In this situation one calcium ion is bound by two oxidized fructose units.

NMR conformational study

a. An example of a ^{13}C NMR spectrum is presented in Fig. 6.

From quantitative ^{13}Cmeasurements using a known amount of t-butanol as internal standard the amount of dicarboxylate was found to be 65 ± 7%, which value is somewhat lower than follows from the chemical analysis.
Based on an Attached Proton Spectrum the signals are assigned as follows:

δ 180 -175.7 ppm COOH groups, δ 104 -105.3 ppm C_5, δ 71 -83 ppm C_2, δ 64 -66 ppm $C_1 + C_6$; C_5 is found in two different and C_2 in many different surroundings. There is evidence that the signals of C_5 and C_2 are somewhat larger than those from the carboxylate groups. This may be attributable to the contribution of the non-oxidized units.

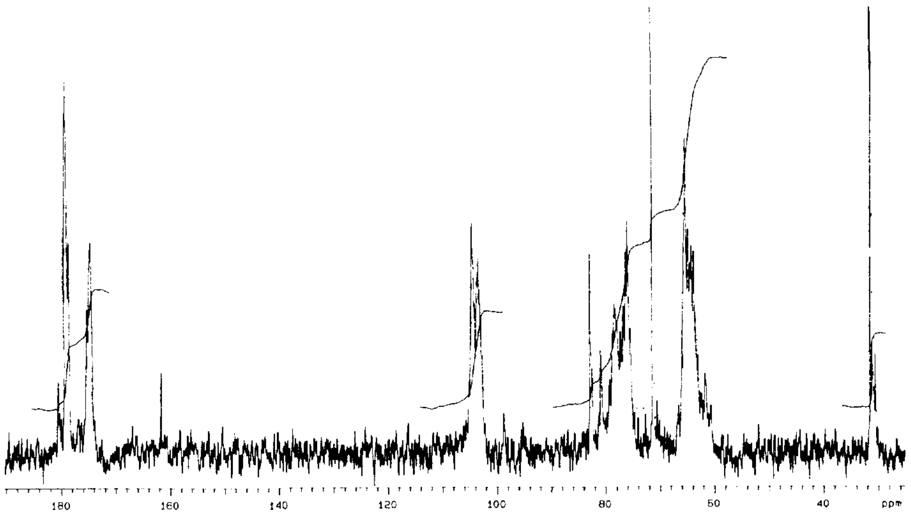

Fig. 6. ^{13}C NMR spectrum of dicarboxy-inulin as disodium salt in D_2O (sample from a preparation described in chapter 3, Table 2, experiment 2).

b. By ^{17}O NMR spectroscopy the number of coordinating water molecules has been determined in the high DCI/Ca region using Dy(III) as a model for Ca. The Dy(III) induced shifts of the ^{17}Owater resonance in the presence and absence of dicarboxy-inulin were measured. The measurements are given in Fig. 7.

In the presence of dicarboxy-inulin the slope of the plot of the induced shift versus the molar ratio Dy(III)/ H_2O ρ is 2495 ppm. Because the slope in the absence of organic ligands in pure $D_2O$is 18800 ppm and Dy(III) binds 8 molecules of water the shift per D_2O molecule is 2350 ppm. From this it follows that in the presence of dicarboxy-inulin one water molecule is coordinated by 1 molecule of Dy. Hence it is concluded that dicarboxy-inulin provides 7-8 coordinating sites for Dy.
Because of the similarity of dysprosium and calcium with respect to their coordinating behaviour it is expected that calcium ions also will be bound by 7- 8 oxygen atoms of the dicarboxy-inulin molecule.

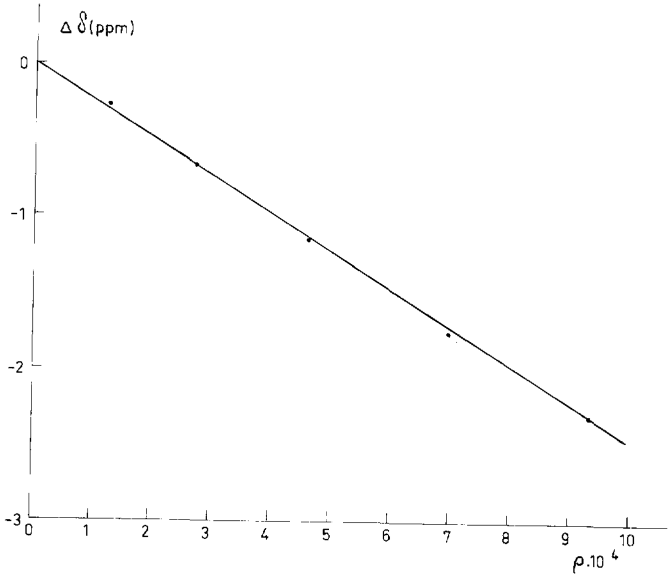

Fig. 7. Dy(III) induced shift of the ^{17}O resonance of water (C $_{dicarboxy-inulin}$ = 0.18 M), 288 K, pH 7.0 (ρ = mole Dy(III) per mole D_2O).

c. A ^{13}C relaxation study was carried out with the aim to establish which O atoms are involved in the coordination of calcium. To a solution of 68.2 mg of dicarboxy-inulin (420-600 μmole carboxylate groups) in 0.5 ml D_2O known amounts of a 11.2 mM Gd(III) solution were added. By longitudinal ^{13}C spectroscopy (T_1) the relaxation time of the respective C-atoms in DCI was measured as a function of the Gd(III) concentration. The results of these measurements are summarized in Table 1.
If it is assumed that the mean residence time of the dicarboxy-inulin ligand in the Gd(III) complex is short with respect to the longitudinal relaxation time of the complex, the relaxation time is inverse proportional to r^6,(r =distance C-Gd(III)). It is concluded that all carbon atoms are influenced by the coordination with Gd with the exception of C_2. This is difficult to understand because of the small relaxation

rate enhancement of the signal at 71-83 ppm and the high relaxation rate enhancement of the carboxylate groups, indicating that the latter are bound to Gd(III). One should expect that the relaxation time of C_2, being proximate to the carboxylate group will be enhanced too. It is however possible that C_2 signals of non-oxidized units, which have a longer relaxation time interfere, resulting in a seemingly longer residence time. All oxygen atoms with the exception of those present in the backbone oxygen atom seem to participate in the coordinating of Gd(III) by dicarboxy-inulin. The distance from this ion to the central ion seems to be longer, as judged from the relaxation time .

Table 1. The reciprocal longitudinal relaxation time ($1/T_1$) as a function of the Gd(III) concentration.

nM Gd(III)	C_3/C_4	C_3/C_4	C_5	C_5	C_2	C_1/C_6
0	0.440	0.289	0.226	0.267	2.036	4.926
224	2.577	1.748	1.244		5.525	6.622
448	5.556	5.348	2.227	4.348	5.645	7.874
672	7.812	6.250	3.195	6.098	6.757	8.850
896	9.434	11.36	4.859	8.772	6.662	10.42
Slope[1]	*0.116*	*0.133*	*0.056*	*0.104*	*0.0218*	*0.065*

[1] *($1/T$ vs. $C_{Gd(III)}$).*

d. Attempted calcium, yttrium and lanthanide NMR spectroscopy did unfortunately not result in interpretable results, amongst others due to precipitation or broad, not interpretable signals. Hence conformational changes at various metal ion concentration could not be measured.

The results for dicarboxy-inulin with Ca(II), present in relatively high concentration indicate a configuration in which one oxidized fructose unit per Ca(II) is involved and probably an ODA-structure is formed (see Fig. 8).

At a low Ca(II)-dicarboxy-inulin ratio a new configuration will be formed in which two oxidized fructose units participate. As mentioned above a helical structure in the coordination of dicarboxy-starch has been postulated to explain such a behaviour. A helical structure of dicarboxy-inulin with calcium coordination as proposed in the coordination of calcium with dicarboxy-starch two oxidized moieties, each with two carboxylate groups cannot be excluded. A situation in which seven donor sites are available, is created in a dicarboxy-inulin molecule when the calcium ion is located

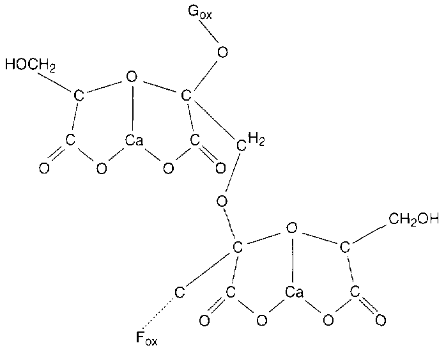

Fig. 8. Proposal for the structure of a 1:1 DCI-Ca complex.

between two adjacent oxidized fructose-units. In this conformation binding of the calcium ion to one of the primary alcohol groups seems to be not possible, because of steric reasons. The possibility that another CH_2OH-groupis bound to another adjacent moiety should be considered.

A strainless conformation can be visualized from a physical (Stuart) model in which two adjacent oxidized fructose units provide 6 cooperating coordination sites.

Another possibility is found when two oxidized fructan units each from a different molecule, coordinate one Ca-ion. In such a case the formation of layered polymer molecules occurs via the calcium ion as proposed for the calcium binding of pectins, known as the egg-box model [14]. Finally the possibility should be considered in which two oxidized fructose units at random bind one Ca(II) ion. Such a situation may even arise when a cyclic or helical form is obtained.
Especially the latter case, one Ca(II) bound by two oxidized fructose units, is interesting because of the new conformation which allows this behaviour, each providing one oxidized fructose unit. In Figure 9 a proposal is given. In this situation Ca(II) is coordinated by 6 O-atoms.

Conclusion

The results of this study provide evidence that two kinds of complexes may be formed between dicarboxy-inulin and Ca(II):

1. at a high calcium-dicarboxy-inulin ratio (i.e. 0.5:1 - 1:1) one Ca(II) is bound by one oxidized fructose unit. The most likely conformation seems to be given that each ODA-unit coordinates one Ca(II) ion

2. at a low calcium-dicarboxy-inulin ratio (i.e. < 0.5 : 1) one Ca(II) is bound by two oxidized fructose units.

Evidence for the latter situation follows from the behaviour upon complexation with Ca(II), as can be seen from the changes of the complex constant and from the changes observed in the optical rotation as a function of the Ca(II)/ligand ratio.
Four possibilities can be envisaged:

- two non-neighbouring dicarboxy groups of one inulin chain coordinate one Ca(II) ion (helix or ring type)
- two adjacent dicarboxy-fructose units coordinate one Ca(II) (cage type)
- two dicarboxy-units of different chains cooperate in binding Ca(II)
- regular binding of two chains (egg-box or double helix type).

Because of the lack of data as yet no definite conclusions can be drawn regarding this conformation.

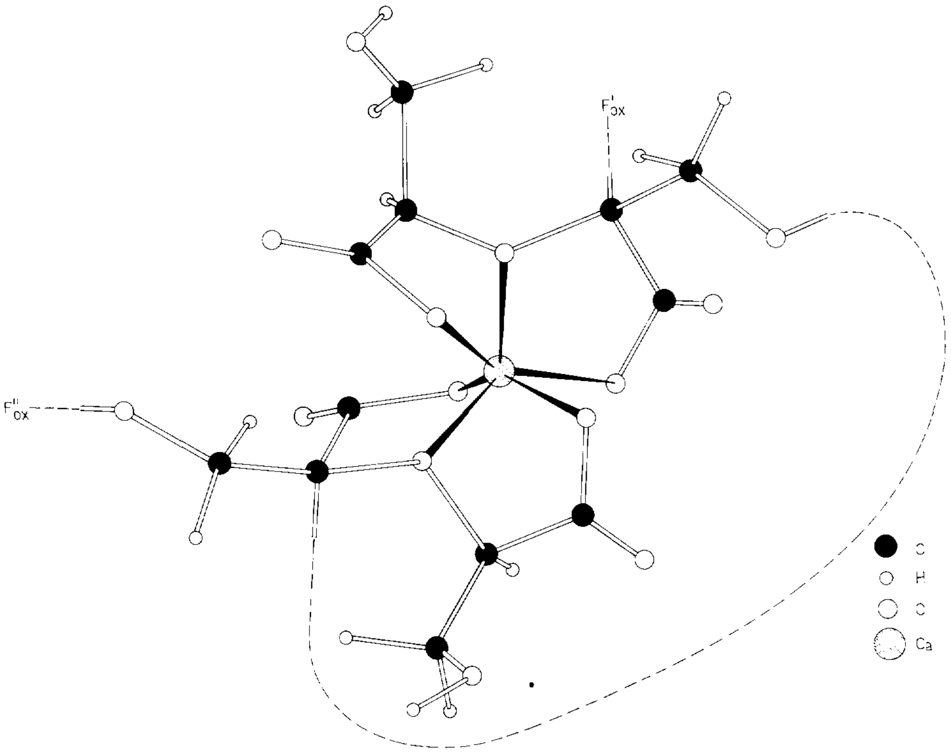

Fig. 9. Proposal for a 1:2 DCI-Ca complex. Two oxidized fructose units provide 6 coordination sites.

Acknowledgement

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CHAPTER 8

SOME ENVIRONMENTAL AND ECONOMIC CONSIDERATIONS ON THE USE OF DICARBOXY-STARCH AND DICARBOXY-INULIN AS BUILDERS IN DETERGENT FORMULATIONS

Introduction

In the foregoing chapters of this thesis it is described that both starch and inulin can be converted by simple reactions into materials which because of their calcium binding capacity may be used as builder or co-builder in laundry detergents. Because various methods for the preparation of dicarboxy derivatives are available, it is desirable to consider the respective reactions and the consequences for the price of the product and application, taking into account the performance and also the environmental impact. The latter aspect covers the consequences of a large-scale production as well as the release of the material into the (aqueous) environment.

Three processes for the production of dicarboxy-starch and two processes for the production of dicarboxy-inulin seem to be feasible in technical and economical sense.

Starch as raw material

a. Two step procedure

Starch, amylose, amylopectin, malto- and cyclodextrins can be oxidized in two steps with $NaIO_4/NaClO_2$ [1, 2].

This method is only feasible if in a large-scale process the first step will be carried out electrochemically. The second step is assumed to be carried out according to the method modified by *Floor* et al. [1]. The amount of $NaClO_2$ needed (6 molecules per glucose unit) is reduced by using the combination $NaClO_2/H_2O_2$.
In the reaction sequence

$$\text{dialdehyde starch} + 2\,NaClO_2 \rightarrow \text{dicarboxy-starch} + NaOCl$$

$$2\,ClO_2^- + HOCl \rightarrow 2ClO_2 + Cl^- + OH^-$$

the reagent decomposes. The decomposition of the reagent is prevented by using hydrogen peroxide:

$$NaOCl + H_2O_2 \rightarrow NaCl + O_2 + H_2O$$

Important features of this process are:
- the high performance of the product (sequestering capacity[1] up to 2.5 mmole Ca/g)
- a high production price, even if regeneration of sodium periodate by electrochemical means is applied
- the necessity to produce a low molecular weight product in order to obtain biodegradable material i.e. the starch has to be depolymerized partly, which may occur in any stage of the process
- the large salt burden
- a two (or even three) step-procedure.

b. One step procedure (dicarboxy-starch prepared with sodium hypochlorite/ sodium bromide [2-4]).

The reactions are as follows:

$$NaBr + NaOCl \rightarrow NaOBr + NaCl$$

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[1] The calcium sequestering capacity is defined as the number of mmole Ca(II), that will be bound by one gram of sequestering agent at pH 10-10.5 until the concentration of non-bound Ca(II) is 10^{-5} M. This value is considered to be the upper limit in the washing process at which practically no incrustation occurs.

starch + 3 NaOBr → dicarboxy-starch + 3 NaBr

Characteristic for this process are:

- use of a cheap reagent
- large salt burden
- one step procedure.

c. One step procedure (dicarboxy-starch prepared via an indirect electrochemical oxidation)

The reaction is similar to that mentioned in 1b.
The bromide is electrochemically oxidized, yielding NaOBr/HOBr, with as consequence that only a limited amount of this material is needed. The characteristics of a process for the preparation of materials using this method are:

- relatively expensive electrochemical apparatus needed
- low-cost of chemicals (only limited amounts of NaBr are required)
- low salt burden.

Inulin as raw material

For the production of dicarboxy-inulin only two processes are of importance, because the $NaIO_4/NaClO_2$ oxidation does not seem to be feasible [1, 6].

a. Oxidation with hypochlorite [4]

By analogy with the oxidation of starch the characteristics for this process are:

- cheap reagent
- large salt burden
- one step procedure.

b. Electrochemical oxidation

The same characteristics hold as those mentioned in Ic:

- expensive electrochemical apparatus needed
- low-cost of chemicals (only a small amount of NaBr)
- low salt burden.

Estimate of the price of dicarboxy-starch and dicarboxy-inulin

Starch and inulin differ beside the chemical properties in two important aspects: the availability and connected with this the price.

Starch is produced in large quantities and has a low price. So far inulin is produced only in moderate quantities and as a consequence has a higher price than starch. This is expected to change rapidly; moreover, the calcium binding performance of dicarboxy-inulin, obtained via the hypochlorite oxidation is equal to that of dicarboxy-starch prepared using the $NaIO_4/NaClO_2$ method. In order to quantify these data a survey of the estimated costs and sequestering capacity of the respective products is given in Table 1. The estimate of the costs, as given in Table 1 is based on several assumptions. Apart from this we have calculated the price of dicarboxy-inulin for various scenarios in which prices of NLG 2-4 /kg inulin are considered (see Table 4)[1].

Environmental and energetic aspects

A second aspect concerns the environmental impact of the production and the measures which can be taken to protect the environment.

A survey of the environmental impact is given in Table 2.

Because of the minor importance of the energy aspects (CO_2, NO_x),these are neglected.

In Table 3 a survey of the price of dicarboxy-starch including estimated costs of processing and work-up, the performance and the price/performance ratio are given. Table 4 gives the estimated prices of dicarboxy-inulin at various prices of inulin.

From these estimates one should conclude that oxidized inulin offers the best perspectives for usage as builder or co-builder in detergents, provided the future price of the raw material will be low. This has to be attributed to its relatively good calcium binding properties. However, an important prerequisite is that the material is biodegradable. The prospects for partially oxidized inulin are good, but so far no reliable data about the biodegradability of the fully oxidized products are known. Therefore one has to account for the possibility that fully oxidized products are not applicable and that as a consequence lesser performing (and somewhat cheaper) products should be applied.

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[1] It may be noted that meanwhile a Belgian company and a Dutch-Belgian joint venture have started inulin production on a substantial scale.

Table 1. Estimated price of dicarboxy-starch and dicarboxy-inulin.

Process	Chemicals/ energy	Amount (kg or kWh)[1]	Price of chemicals/energy (NLG)	Yield[2] (%)	Total costs[3] (NLG)	Price per kg (NLG)
1a.	starch	1	1.20	80	a. 9.25	9.60
	NaIO4	-	-		b. 1.25	
	kWh	0.8	0.15			
	$NaClO_2$	1	6.60			
	H_2O_2	0.15	0.60			
	NaOH	0.40	0.70			
1b.	starch	1	1.20	90	a. 4.45	3.80
	NaOCl	1.35	2.25		b. 0.50	
	NaOH	0.5	0.75			
	NaBr	0.05	0.25			
1c.	starch	1	1.20	90	a. 2.95	3.00
	NaBr	0.05	0.25		b. 1.00	
	NaOH	0.50	0.75			
	kWh	3.6	0.75			
2a.	inulin	1	4.00	90	a. 7.25	6.00
	NaOCl	1.35	2.25		b. 0.50	
	NaOH	0.50	0.75			
	NaBr	0.05	0.25			
2b.	inulin	1	4.00	90	a. 5.75	5.20
	NaBr	0.05	0.25		b. 1.00	
	NaOH	0.50	0.75			
	kWh	3.6	0.75			

[1] *Amount needed for the oxidation of 1 kg of (dry) carbohydrate.*

[2] *Calculation of the yield is based on $M = 162$ of the glucan- or fructan moiety and $M = 236$ for the oxidized moiety as disodium salt*

[3] *a. costs of chemicals and electrical energy*
b. estimated process costs.

Another important factor may be the higher molecular weight of dicarboxy-starch, which may give a contribution to the dispersing properties of the detergent. In a limited number of experiments we have established that starch yields a product which despite its low calcium sequestering capacity (0.4-0.6 mmole Ca/g) has a satisfactory performance in washing experiments and is readily biodegradable[1]

Table 2. Some energetic and environmental consequences for the production of dicarboxy-starch and dicarboxy-inulin.

Process	Salt burden (kg NaCl/kg product)	Energy input (electrochemical, kWh)	Prospects for biodegradability[1]
1a.	0.60	0.6	-
1b.	0.80	-	+
1c.	0.05	3.6	+
2a.	0.80	-	±
2b.	0.05 (as NaBr)	3.6	±

[1] *+ Biodegradability has been shown; ± evidence for biodegradability; - poorly biodegradable*

Table 3. Price-performance ratio of DCI/DCS.

Material[1]	Process	Price (NLG)	SC (mmole Ca/g)	Price/performance (NLG /SC)
DCS	1a.	9.60	2.5	3.80
DCS	1b.	3.80	1.3	2.90
DCS	1c.	3.00	1.3	2.30
DCI	2a.	6.00	2.0	3.00
DCI	2b.	5.20	2.0	2.60

[1] *DCS = dicarboxy-starch; DCI = dicarboxy-inulin.*

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[1] according to OECD- guidelines

Table 4. Price and price performance ratio of dicarboxy-inulin (NLG) at various prices of inulin.

Price of inulin[1]	Overall costs of chemicals[1]	Price of DCI[1]	Price/performance[2]
4	5.75	5.20	2.60
3	4.75	4.50	2.25
2	3.75	3.70	1.85

[1] *NLG/kg or NLG for the conversion of 1 kg of dicarboxy-inulin*
[2] *NLG/SC)*

Undoubtedly the experiments need more background and support. Especially the better performing dicarboxy-starch (SC = 1.1 - 1.4 mmole Ca/g) and dicarboxy-inulin should be investigated, preferentially in washing experiments. In anticipation of these results it can be concluded that both oxidized starch and inulin are promising substitutes of phosphate or polycarboxylate in laundry and industrial detergent formulations.

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SUMMARY

In this thesis the results of a study are presented on a new method for the glycol cleavage oxidation of polysaccharides leading to dicarboxy derivatives. This method concerns the bromide-catalyzed hypochlorite oxidation, which has been applied to starch and inulin. Starch oxidized in this way yields 2,3-dicarboxy-starch which because of its calcium sequestering properties may be used as a replacement of sodium tripolyphosphate (STP) or synthetic polycarboxylates in detergent formulations. Inulin yields 3,4-dicarboxy-inulin which, contrary to earlier work, prepared in this way proved to be an excellent calcium binding agent. In this thesis various aspects are discussed of the hypochlorite oxidation and the hypochlorite/bromide system and of the characterization of the products, with special emphasis on dicarboxy-inulin.

Chapter 1 deals with a discussion of advantages and drawbacks of STP and its substitutes nowadays in use as builder in laundry detergents. STP, which is a cheap and effective calcium binding agent has various attractive properties in the washing process, but because the material may contribute to eutrophication of stagnant waters a substitute is desirable. Nitrilotriacetic acid, which is also a very good calcium sequestering agent may be insufficiently biodegradable under certain environmental circumstances and moreover is suspected to be carcinogenic. It is therefore used only to a limited extent. The inorganic ion exchanger zeolite NaA is used on a large and increasing scale in Europe. The material has several attractive properties with respect to calcium binding and toxicity. The slow magnesium binding of zeolite NaA and the bad removal of incrustations on fabrics make the use of a co-builder necessary. Polycarboxylates, of the polyacrylate-type, which are used for this purpose, are non-biodegradable so that a substitute is desirable. Oxidized carbohydrates are considered as candidates for

replacement of these materials because they have a good calcium binding strength and in view of their structure, are expected to be biodegradable. Furthermore they can be prepared from cheap and renewable materials. In view of these prospects there is a demand for cheap preparation procedures. It appears that the process consisting of consecutive oxidation with $NaIO_4/NaClO_2$ yields well-performing high polymeric but poorly biodegradable products. Hypochlorite oxidation yields products with a somewhat lesser performance. Due to the lower molecular weight they are expected to be better biodegradable. The use of bromide as a catalyst offers various advantages, the most important being that generally better performing products are obtained. It appears that both kinetics and mechanisms of the hypochlorite and the hypobromite oxidation of starch are poorly understood. Additional studies on this subject seem therefore desirable. Also an additional study on the preparation and characterization of dicarboxy-inulin is required.

Chapter 2 deals with the hypochlorite/bromide oxidation of starch. The highest yield (95%) and the best performing products, with a sequestering capacity (SC) of 1.3 - 1.4 mmole Ca/g, are obtained when the oxidation is carried out at pH 10 and low temperature. These products have a better performance than the products obtained via the non-catalyzed reaction. When the oxidation is carried out at lower pH (9) and relatively high temperature the yield and the SC are lower. These results may be attributable to either the decomposition of the reagent, resulting in the formation of chlorate, or to side reactions of intermediate products, which are ultimately converted into stable lactones, which are expected to have a low SC.

Chapter 3 gives the results of the investigations directed to the inulin oxidation. The products, obtained in high yield (90%), have a sequestering capacity up to 2.5 mmole Ca/g, which is markedly higher than that of the starch products, prepared in a similar way. The best performing products are obtained at high pH in conformity with the conditions for the oxidation of starch. The explanation for the differences in results in relation to the reaction conditions are similar to those observed for the oxidation of starch i.e. decomposition of $NaOCl/OCl^-$ towards chlorate or formation of lactones will lead to products with a lower degree of oxidation.

In chapter 4 it is noted that if either OCl^- or HOCl is the reactive species the rate of the oxidation of hypochlorite/hypochlorous acid should be pH dependent: the maximum rate should be found at about pH 5 or at pH > 9. Because the optimum is found at pH 7 it is concluded that neither HOCl nor OCl^- are the essential reactive species, but that these probably arise from a reaction of these substances. A computer simulation of the reactions, including the hypothetical reaction of 2 molecules of HOCl with one molecule of OCl^- supports this idea: experimental results over a wide pH range can be predicted accurately. In an annex a survey is given of the reactivity of various classes of substances and a method is described for the prediction of the reactivity of organic compounds towards the OH-radical. It appears that this method applied to carbohydrates gives evidence that the vicinal diol group in a radical mechanism is the most reactive part of the molecule.

In chapter 5 an experimental study is described with the aim to quantify the catalytic role of bromide. The catalytic effect is ascribed to the fast conversion of bromide into hypobromite, which is known to react faster than hypochlorite. Applied to the substrates linear dextrins and inulin, it is found that the consumption of the reagent is linear in time, which proves the catalytic effect of bromide. It is established that the rate is slightly pH dependent. From the results the rate constants for the hypobromite oxidation are calculated. The rate constants are in agreement with those mentioned in literature (for the oxidation of starch).

Chapter 6 gives the results of the investigations concerning the relation between the degree of oxidation of starch and inulin and the Ca-binding ability. The compounds behave quite different in this respect. In the initial phase of oxidation the sequestering capacity of starch increases only to a slight extent until an oxidation degree of 40% is reached. The SC increases then sharply till 65%; further oxidation leads only to a slight increase in SC. Inulin upon oxidation yields products from which the SC increases linearly with the degree of oxidation. The different behaviour is ascribed to the fact that upon oxidation the most suitable configuration for Ca-coordination in inulin is obtained immediately whereas this configuration in starch is only obtained after substantial oxidation.

Chapter 7 describes the experiments with the aim to elucidate the calcium coordination of dicarboxy-inulin (DCI). It is established that the optical rotation of DCI changes linearly with increasing calcium concentration. No further change occurs when a 1 : 2 Ca/DCI ratio is obtained. A similar phenomenon is observed with the complex constant. At high calcium Ca/DCI ratio (> 0.5) the complex constant K is relatively low, but at Ca : DCI $< 0,5$ the complex constant increases sharply. In addition NMR spectroscopy measurements were carried out. ^{17}O NMR spectroscopy measurements of Dy(III)-DCI complexes showed evidence that DCI provides 7-8 coordinating sites. From ^{13}C NMR relaxation rate enhancement measurements of the Gd(III)-DCI complexes, evidence was obtained that (at low metal ion concentration) in the coordination all oxygen atoms, with the exception of those present in the backbone, are involved. The results of this study suggest that two configurations exist. Proposals for some conformations are given.

Chapter 8 gives a survey of the feasible preparation procedures of both dicarboxy-starch and dicarboxy-inulin, the environmental impact of the preparation and large-scale use and of the estimated costs for the production of these materials and their price/performance ratio. It is concluded that both materials may be considered as substitute of phosphate or polycarboxylates in laundry detergents.

SAMENVATTING

In dit proefschrift worden de resultaten beschreven van een onderzoek naar een nieuwe methode om de vicinale diolgroep van koolhydraten te splitsen door oxidatie. Deze methode betreft de volledige oxidatie door middel van hypochloriet met bromide als katalysator. Uit zetmeel wordt 2,3-dicarboxy-zetmeel verkregen dat, zoals bekend is een materiaal oplevert dat calciumbindende eigenschappen bezit en te gebruiken is als co-builder in wasmiddelen. Inuline op deze wijze geoxideerd, levert 3,4-dicarboxy-inuline op dat, in tegenstelling tot het materiaal verkregen door inuline-oxidatie volgens andere methoden, een zeer goede calciumbinder oplevert. Op een aantal aspecten betreffende de hypochloriet/hypobromietoxidatie en de karakterisering van de produkten wordt nader ingegaan, waarbij dicarboxy-inuline speciale aandacht krijgt.

In Hoofdstuk 1 worden de voor- en nadelen besproken van pentanatriumtripolyfosfaat ("fosfaat") en diens vervangers die momenteel in gebruik zijn als builder in wasmiddelen. Fosfaat is een goed calciumbindend middel en bezit daarnaast aantrekkelijke waseigenschappen. Het grote nadeel is dat een teveel aan fosfaat kan bijdragen aan de eutrofiëring van weinig doorstroomde oppervlaktewateren. Daar niet gekozen is voor een fosfaatverwijdering via een derde trap in afvalwaterzuivering, is een reductie van fosfaatlozing vereist.
Nitrilotriazijnzuur is eveneens een goede calciumbinder maar blijkt niet onder alle omstandigheden bioafbreekbaar en is daarnaast verdacht carcinogeen. Het gebruik ervan is dan ook in een aantal landen beperkt.
De anorganische ionenwisselaar zeoliet NaA is een redelijke calciumbinder en is toxicologisch niet verdacht. De langzame magnesiumbinding en slechte verwijdering van incrustaties van het wasgoed tijdens het wasproces maken het gebruik van een co-builder

noodzakelijk. Hiervoor worden thans synthetische polycarboxylaten van het acrylaattype gebruikt, die echter niet afbreekbaar zijn en waarvoor een vervanger dan ook wenselijk is. Geoxideerde koolhydraten komen hiervoor in aanmerking omdat ze goede calciumbinders zijn en, vanwege het voorkomen van acetaal- en ketaalfuncties, naar wordt verwacht, wel afbreekbaar zijn. In verband met deze vooruitzichten is er een vraag naar een goedkope bereidingswijze van deze materialen. Het proces waarin men een polysaccharide achtereenvolgens oxideert met $NaIO_4$ en $NaClO_2/H_2O_2$, heeft als voordeel dat de produkten weliswaar een goede calciumbindende capaciteit bezitten, maar als belangrijk nadeel dat ze niet of niet voldoende afbreekbaar zijn. Oxidatie met hypochloriet levert produkten met een mindere werking, maar tengevolge van het lagere moleculair gewicht zijn deze waarschijnlijk wel afbreekbaar. Het gebruik van bromide als katalysator heeft enkele gunstige invloeden; vooral de kwaliteit van het produkt blijkt beter.

Uit de literatuur blijkt dat zowel het mechanisme als de kinetiek van de hypochloriet- en hypobromietoxidatie slecht wordt begrepen, zodat op dit gebied aanvullende onderzoekingen gewenst zijn. Ook dicarboxy-inuline, dat op deze wijze is bereid, dient nader te worden gekarakteriseerd.

Hoofdstuk 2 beschrijft de oxidatie van zetmeel door middel van de hypochloriet-bromide methode. Dicarboxy-zetmeel wordt in een opbrengst van ca. 90% verkregen. Het sequestrerend vermogen (SC) blijkt hoger te zijn dan van het materiaal dat zonder bromide is bereid. De beste resultaten worden verkregen bij pH 10 en lage temperatuur (SC = 1,4 mmole Ca/g). Een en ander laat zich verklaren uit het feit dat bij relatief lage pH en hoge temperatuur de ontleding van hypochloriet/hypobromiet wordt bevorderd, hetgeen nadelig is voor het bereiken van een voldoende hoge oxidatiegraad of uit de mogelijkheid dat bij lage pH stabiele intermediairen worden gevormd.

In hoofdstuk 3 wordt nader ingegaan op de oxidatie van inuline. Dicarboxy-inuline wordt in hoge opbrengst (90%) verkregen; het materiaal vertoont een zeer goede calciumbinding (SC = 2,5 mmole Ca/g). De optimale omstandigheden zijn hetzelfde als bij oxidatie van zetmeel. Ook de verklaring hiervan is gelijk aan die hierboven voor zetmeel is beschreven: disproportionering van het oxidant of vorming van lactonen leidt tot een lagere oxidatiegraad.

Hoofdstuk 4 signaleert het feit dat de hoogste reactiesnelheid van de oxidatie van zowel cellulose als zetmeel bij pH 7 wordt gevonden terwijl de verantwoordelijke reactiecomponenten hier niet in de hoogste concentratie voorkomen. Dit laat zich verklaren door aan te nemen dat uit een reactie van HOCl en OCl^- reactieve deeltjes (radicalen of vrije atomen) ontstaan en dat deze reactie snelheidsbepalend is. Een computersimulatie waarin onder meer deze hypothetische reactie is opgenomen, geeft over een breed pH gebied een goede overeenstemming te zien tussen experimentele en berekende waarden. In een aanhangsel wordt nader ingegaan op de consequenties van een radicaalmechanisme. Op basis van literatuurgegevens blijkt het mogelijk een voorspelling te doen omtrent de reactiviteit van de verschillende structuuronderdelen in een organische verbinding. Volgens deze methode, toegepast op respectievelijk de anhydroglucose- en fructoseeenheid van zetmeel en inuline, blijkt de diol groep het meest reactieve deel van de groep te zijn. Geconcludeerd wordt dat een radicaalreactie de selectiviteit van de oxidatie verklaart.

Hoofdstuk 5 is gewijd aan het vaststellen van de katalytische rol van bromide. Dit effect wordt toegeschreven aan de omzetting van bromide in hypobromiet dat sneller met koolhydraten reageert dan hypochloriet. Uit de experimenten blijkt de reactiesnelheid evenredig toe te nemen met de bromideconcentratie. De uit de experimenten afgeleide reactieconstante (voor zowel lineaire dextrinen als inuline) blijkt overeen te komen met de in de literatuur vermelde waarde voor zetmeel.

De relatie tussen sequestrerend vermogen en de oxidatiegraad van respectievelijk zetmeel en inuline wordt in hoofdstuk 6 behandeld. Deze twee stoffen blijken zich verschillend te gedragen. Het sequestrerend vermogen van zetmeel neemt bij oxidatie aanvankelijk slechts in geringe mate toe, totdat een oxidatiegraad van ca. 40% is bereikt. Het SC neemt sterk toe tot een oxidatiegraad van ca. 65%, waarna deze grootheid nog slechts geleidelijk toeneemt.

Bij inuline wordt waargenomen dat het SC lineair toeneemt met de oxidatiegraad. Het verschil in gedrag van deze twee stoffen wordt toegeschreven aan het feit dat bij zetmeel de meest geschikte configuratie voor calciumcomplexering pas wordt bereikt als twee naast elkaar gelegen glucose-eenheden zijn geoxideerd, terwijl bij inuline deze structuureenheid rechtstreeks wordt verkregen uit elke fructose-eenheid.

Hoofdstuk 7 beschrijft de resultaten van een onderzoek naar de achtergrond van de calciumcomplexering van dicarboxy-inuline (DCI). Door toevoeging van calcium verandert de optische rotatie van DCI. Tussen een verhouding calcium/DCI 0:1 (mol/mol) tot 0,5:1 blijkt de verandering lineair te zijn. Bij een hogere calcium/DCI verhouding verandert de draaiing echter niet verder. Zoals wordt verwacht, blijkt ook de complexconstante af te hangen van deze verhouding (beladingsgraad). Bij aanwezigheid van relatief veel calcium is de complexconstante K laag. Bij afnemende Ca/DCI verhouding (< 0,5) neemt de waarde van K toe. Uit een NMR-studie die is uitgevoerd met de aan calcium verwante gadolinium- en dysprosiumionen volgt dat bij lage ion/DCI verhouding deze ionen door 7- 8 zuurstofatomen van dicarboxy-inuline worden gebonden, zodat geconcludeerd moet worden dat het centrale ion omringd is door twee geoxideerde fructose-eenheden. Niet geheel duidelijk is hoe deze conformatie tot stand komt. Enkele plausibele mogelijkheden worden aangegeven.

Hoofdstuk 8 geeft een vergelijking van de prestaties van dicarboxy-zetmeel en dicarboxy-inuline en een schatting van de kostprijs. Gebaseerd op de prijs/prestatie verhouding is het te verwachten dat beide stoffen als (co)-builder te gebruiken zullen zijn. Een belangrijke voorwaarde zal echter de biodegradeerbaarheid zijn. Dicarboxyzetmeel blijkt volgens een OECD-toets readily-inherently biodegradable te zijn. Uit enkele experimenten volgen sterke indicaties dat ook DCI biodegradeerbaar is. De overige milieuconsequenties voor fabricage en benutting van grondstoffen lijken gering. Zowel geoxideerd zetmeel als geoxideerd inuline komen derhalve in aanmerking als fosfaat- of polycarboxylaatvervanger in wasmiddelen.

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Promoveren is omzien in rok. Deze aardige stelling heeft een promovendus enkele jaren geleden aan zijn proefschrift toegevoegd en wellicht verdedigd. Het omzien geldt in de eerste plaats uiteraard het vele werk dat verzet moest worden om een dun boekje te produceren. Het omzien is in belangrijke mate ook naar diegenen die direct of indirect en in meer of mindere mate hebben bijgedragen aan de totstandkoming ervan.
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CURRICULUM VITAE

Arie Cornelis Besemer werd in 1944 te Schiedam geboren. Na het behalen van het HBS-B diploma in 1961 trad hij in dienst van de Nederlandse organisatie voor toegepast natuurwetenschappelijk onderzoek TNO. In 1962 werd met goed gevolg het examen voor het eerste deel Analist en in 1964 het tweede deel Analist (Organische Chemie) afgelegd. In 1971 werd aan de Rijksuniversiteit te Utrecht het diploma A natuur- en scheikunde behaald. Hierna werd de militaire dienstplicht vervuld.
Bij TNO was hij achtereenvolgens werkzaam op het gebied van organische synthese van radio-actief gemerkte verbindingen, organische elektrochemie en milieuchemie (bestudering van omzettingen van verbindingen in de atmosfeer). Momenteel is hij werkzaam bij de afdeling Biochemie en Fysische Chemie van het Instituuut voor Biotechnologie en Chemie (TNO-Voeding), waar hij onderzoek verricht naar chemische en enzymatische omzettingen van o.a. koolhydraten.