Carbohydrate Polymers 84 (2011) 1110–1116

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Hydrophobically modified inulin from alkenyl succinic anhydride in aqueous media

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ARTICLE INFO

Article history:
Received 24 November 2010
Received in revised form
22 December 2010
Accepted 23 December 2010
Available online 8 January 2011

Keywords:
Inulin
Hydrophobic polysaccharides
Synthesis
Hydrophobic modification
Esterification
Micellar catalysis

ABSTRACT

Medium and long chain esters of inulin have been prepared by reaction of alkenyl succinic anhydrides (ASA) such as 2-octen-1-ylsuccinic anhydride (OSA), and 2-dodecen-1-ylsuccinic anhydride (DDSA) in aqueous media and aqueous surfactant media, respectively. The design of the chemical process was based on the study of the influence of several reaction parameters on reaction efficiency (estimated by ^{1}H NMR analysis of the pure end product) and reaction time. Inulin concentration, pH range, temperature, and the addition of a cationic surfactant such as dodecyltrimethylammonium bromide (DTAB) to the reaction media were evaluated for both OSA and DDSA anhydrides.

Inulin slurry aqueous systems were found the best reaction media to carry out the esterification with OSA. In case of DDSA, the addition of a cationic surfactant such as DTAB was required to convert 65% of anhydride. Inulin precipitation was prevented at pH range 8.5–9.0 by the addition of DTAB. The reaction time for the synthesis of dodecenyl succinic esters of inulin, estimated as the total time required to consume all DDSA, was reduced dramatically from 24 h (without DTAB) to less than 1 h in presence of cationic surfactant. The use of micellar basic catalysis resulted in a useful way to obtain long chain alkenyl succinic esters of inulin.

1. Introduction

Inulin extracted from chicory (*Chicorium intybus*) is a non branched polydisperse fructan that mainly consists of β(2 → 1) linked anhydrous fructose units (AFU) and has unique properties due to its linear structure (only 1–2% β(2 → 6) branched). Inulin also contains minor amounts of fructans (F), in which the glucosyl end is not present. Fig. 1 illustrates the structure of inulin (De Bruyn, Alvarez, Sandra, & Leenheer, 1992). This renewable biopolymer has low molecular weight range in comparison to other polysaccharides such as cellulose and starch. The degree of polymerization (DP) of chicory inulin ranges mainly from 2 to 60 and the weight average DP is around 10–14 AFU. Extracted inulin can be further purified to different DPs for different commercial purposes. Viscometry methods and TEM analysis in solution showed that inulin forms supramolecular aggregates of different size and type depending on the ionic strength and the polarity of solvent (Dan, Ghosh, & Moulik, 2009). Globular aggregates were found to be 1.03×10^6 g/mol and 2.4×10^6 in pure aqueous solution and 0.5 M NH_4SCN, respectively, whereas rod-like aggregates of inulin where found in DMSO by the TEM study.

Hydrophobically modified inulins are grafted water soluble copolymers with hydrophobic chains. They are used commercially and represent an important alternative for purely petrochemical-based polymeric surfactants involved in many colloidal systems such as oil in water (emulsions) and solid in liquid stabilizers (dispersions) (Nestor et al., 2008; Tadros, 2009). These amphiphilic biodegradable polymers obtained from inulin have been prepared efficiently by reacting fatty acid chlorides, fatty acid methyl esters, aliphatic anhydrides, alkyl epoxides or alkyl isocyanates using organic solvents as reaction media (Rogge, Stevens, Colpaert, Levecke, & Booten, 2007; Stevens et al., 2001) or in the absence of solvent (Ehrhardt, Haji Begli, Kunz, & Sheiwe, 1999). However, there are many potential advantages of replacing organic solvents with water; the most obvious are cost, operational simplicity and environmental safety. Therefore, to develop new water reaction conditions while maximizing reaction efficiency in water media and reducing reaction time has become of great interest. In line with this matter, the synthesis of β-hydroxyalkyl ethers of inulin was described recently in aqueous media (Morros, Levecke, & Infante, 2010a) and in aqueous surfactant media (Morros, Levecke, & Infante, 2010b).

The aim of this work was to prepare octenyl and dodecenyl succinic esters of inulin (Fig. 2) with a degree of substitution (DS) between 0.05 and 2 under mild alkaline conditions by reaction of alkenyl succinic anhydrides (ASA) such as 2-octen-1-ylsuccinic

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doi:10.1016/j.carbpol.2010.12.077

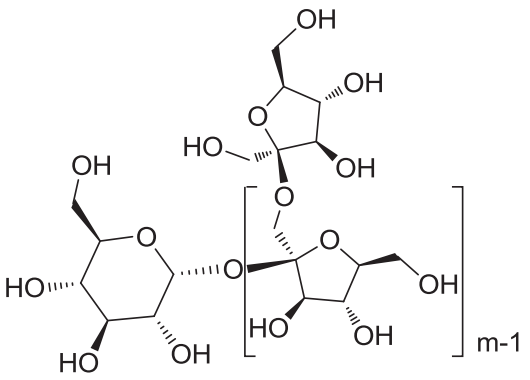


Fig. 1. Main chemical structure of inulin (GF_m) where G corresponds to the glucosyl unit, F to the fructosyl unit and *m* to the degree of polymerization of β(2 → 1) linked fructosyl units (AFU).

anhydride (OSA), and 2-dodecen-1-ylsuccinic anhydride (DDSA) in aqueous media and aqueous surfactant media, respectively. Octenyl and dodecenyl succinic esters of inulin are expected to be more biodegradable compounds than β-hydroxyalkyl inulin ethers already described due to easy cleavage of the ester bond (Morros et al., 2010a, 2010b). Moreover, the introduction of several carboxylic groups with hydrophobic chains into the inulin backbone could yield interesting new inhibitors for calcium carbonate precipitation that are more environmentally acceptable (Akin, Öner, Bayram, & Demadis, 2008). Preliminary results indicated that these new polymeric surfactants have pH sensible emulsification properties.

The first polysaccharide modified with ASA was synthesized from starch using aqueous or organic media (Caldwell & Wurzburg, 1953). Since then, studies on several other polysaccharides, including inulin, were performed with slight variations in reactions conditions and purification methods (Ward, 2002).

In this paper In-ASA modifications were carried out by base catalyzed addition of ASA to an inulin water system. The effect of inulin concentration, the pH range, the reaction temperature and the chain length of ASA in aqueous media were evaluated. Furthermore, the remarkable increase in reaction rate and efficiency experimented with long chain etherification of inulin with 1,2-alkylepoxides in surfactant media (Morros et al., 2010b) encouraged us to apply similar reaction conditions to the esterification with the more hydrophobic anhydride, DDSA. The design of the chemical process was based on the study of the influence on reaction efficiency (RE) estimated by ^{1}H NMR analysis of the pure end product and on reaction time established through the reaction pH.

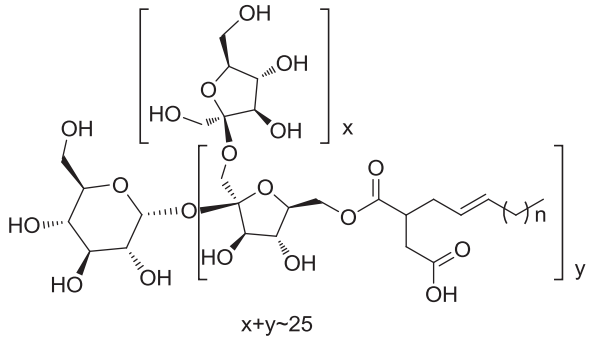


Fig. 2. Structure of alkenyl succinate of inulin (In-ASA) synthesized: 2-octen-1-yl-succinate of inulin (In-OSA, *n* = 4) and 2-dodecen-1-yl-succinate of inulin (In-DDSA, *n* = 8).

2. Experimental

2.1. Materials

The purified inulin, INUTEC® N25, with a main degree of polymerization of about 25, was supplied by ORAFTI Bio Based Chemicals (Tienen, Belgium) at present BENEO-BBC (Beneo®: trade name for inulin products available from ORAFTI, Belgium). The purified inulin, with an average DP of 25, contained a maximum of 0.5% glucose, fructose and sucrose, and a maximum of 5% oligofructose of DP 3–9 in total (% weight calculations are based on total carbohydrate dry substance). It was dried at 70 °C 24 h before use. The following reagents were used for the hydrophobic modification of inulin: 2-octen-1-yl-succinic anhydride (OSA), 2-dodecen-1-yl-succinic anhydride (DDSA), +95%, mixture of cis/trans from Aldrich (St. Quentin Fallavier, France). The surfactant used was dodecyltrimethylammonium bromide (DTAB) supplied from Aldrich (St. Quentin Fallavier, France). Other chemicals were used as received without further purification. Deionized water from our lab was used for all the experiments.

All reactions were carried out in a 50 mL three-neck round-bottom flask. A heating magnetic stirrer (IKA® RCT-Classic) provided with its contact thermometer (IKATRON® ETS-D5) was used to control the reaction temperature inside the reactor. Dialysis tubing was benzoylated (D7884 from Sigma) with an average flat width of 32 mm, a capacity of approximately 100 mL/ft, and a pore size of 2000 Nominal Molecular Weight Cut Off (NMWCO). Deionized water and ethanol (96°) were used for purification through dialysis.

2.2. Analytical methods

HPLC (High performance liquid chromatography) was used to confirm the absence of free hydrolysis by-products in the final inulin ester derivative (using Licrospher 100 CN (5 μm) in ACN/water (2/3) pumped by a Merck-Hitachi L6200 and a UV or RI detector). ^{1}H and ^{13}C nuclear magnetic resonance (NMR) was used to elucidate and characterize all compounds. The analysis was performed at 50 °C, with 30 s of delay between transients, on an Inova 500 MHz or Mercury 400 MHz spectrometer, both from Varian®. Samples were prepared in deuterated dimethylsulfoxide (DMSO-d_6) with trimethylsilane (TMS) as a reference. Chemical shifts were measured in ppm referred to as TMS signal. Also, Fourier transform infrared spectroscopy (FT-IR) was used to elucidate and characterize all compounds. The analysis was recorded on a Nicolet-IR. Samples were prepared with NaBr in a sodium chloride cell.

2.3. General synthesis of octenyl succinate of inulin (In-OSA)

Twenty grams of oven-dried inulin (0.121 mol of AFU) were suspended in 60 mL of deionized water under stirring. The pH was adjusted at the reaction conditions with a pH-meter by adding 1% NaOH solution. OSA (4.6 g, 0.18 equiv. based on AFU) was added drop wise at 25 °C. The pH was maintained at the pH conditions using the same 1% NaOH solution. A pH-meter was used during the reaction to monitor reaction progress. To assure that all OSA was consumed, the end of the reaction was established 1 h after the pH was kept constant. This occurred typically between 4 and 8 h (this value will be considered the reaction time). Once the reaction concluded, the crude was neutralized with 5% HCl solution to a pH of 6.0. The reaction mixture was dialyzed against 50% EtOH/H_2O and water. The resulting dialyzed suspension was freeze dried and a white dried power corresponding to the modified In-OSA was obtained. Control of absence of free OSA species in the final product was checked by HPLC. A white powder was obtained with a

Table 1
RE for the In-OSA modification in water at different inulin concentrations and pH ranges.

Reaction	% Inulin (w/w)	ΔpH	Time (h)	RE (%)[a]	RE′ (%)[b]
1	35	8.5–9.0	4	56 ± 38	–
2	20	9.0–9.5	5	78 ± 5	71 ± 9
3	20	8.5–9.0	6	88 ± 5	80 ± 10
4	20	8.3–8.5	8	94 ± 2	–
5[c]	20	8.3–8.5	24	35 ± 5	–

Reaction conditions: OSA/AFU molar ratio of 0.18; temperature, 25 °C.
[a] DS determined by NMR method, average of three experiments.
[b] DS determined by titration method, average of three experiments.
[c] In-DDSA modification.

yield of 80%. Details of the synthesis and reaction efficiencies are depicted in Table 1.

2.4. General synthesis of dodecenyl succinate of inulin (In-DDSA)

Four grams of oven-dried inulin (24.7 mmol, AFU) were dissolved in 12.0 mL 1 M KOH aqueous solution and 0.010 g $NaBH_4$ (0.3 mmol; 0.01 equiv. based on AFU) under vigorous stirring at 25 °C into a 25 mL round-bottom flask. Then, 0.76 g of DTAB (2.6 mmol; 0.1 equiv. based on AFU) were added to the reaction mixture. After 30 min of stirring, the temperature and pH was adjusted at the reaction conditions, this later with a pH-meter by adding 25% HCl solution. DDSA (1.0 g, 0.15 equiv. based on AFU) was added drop wise at 55 °C. The pH was maintained at the pH conditions using the same 3% NaOH solution. To assure that all DDSA was consumed, the end of the reaction was established 10 min after the pH was kept constant at 9.00. The reaction time for this reaction was around 1 h. Once the reaction concluded, the crude was neutralized with 5% HCl solution to a pH of 6.0. The reaction mixture was dialyzed against 50% EtOH/H_2O and water. The resulting suspension was passed through a strong cationic exchange column (high S support) to remove the remaining cationic surfactant and was finally freeze dried. Control of the absence of free DDSA species in the final product was also checked by HPLC. A white powder was obtained with a yield of 80%. Details of the synthesis and reaction efficiencies are depicted in Table 2 and Figs. 3 and 5.

2.5. Product characterization

The characterization of In-ASA esters was performed on the basis of their degree of substitution (DS) which is defined by the number of alkenyl chains per fructose units. After purification of the end products, the DS of In-OSA and In-DDSA were estimated from a comparative analysis of ^{1}H NMR signals (500 MHz, 30 mg mL^{-1} in DMSO-d_6, 50 °C) of the alkenyl chains and fructose units with less than 10% of fault (Rogge et al., 2007). See supporting information.

Alternatively the DS of In-OSA was also estimated by titration method (Shogren, Viswanathan, Felker, & Gross, 2000). One gram of In-OSA was accurately weighed and dissolved in 10 mL of deionized water by stirring for 10 min at 40 °C. The acid groups of modified inulin were completely ionized by the addition of 0.05 mol/L NaOH solution until a pH of 9.00. Then, all of the basic groups of In-OSA were titrated with 0.05 mol/L standard HCl solution, using a pH-electrode. A blank was simultaneously titrated with native inulin as a control. The DS was calculated as follows with less than 20% of fault:

$$\mathrm{DS} = \frac{\mathrm{MW_{AFU}}}{(W_{\mathrm{SAMPLE}}/CV) - \mathrm{MW_{ASA}}}$$

where MW_{AFU} is the molecular weight of anhydrous fructose units (162 g/mol), MW_{ASA} is the molecular weight of the corresponding alkenyl succinic anhydride and the W_{SAMPLE}, C and V are the dried sample weight, the molarity of HCl solution and the volume used during the titration, respectively. The esterification of inulin by ASA was also confirmed using ^{13}C NMR and FT-IR spectroscopy. See supporting information.

Table 2
RE for the In-DDSA modification in DTAB–H_2O system at different pH ranges.

Reaction	ΔpH	RE (%)[a]
6	8.3–8.5	41 ± 5
7	8.5–9.0	54 ± 5
8	9.0–9.5	37 ± 5

Reaction conditions: inulin concentration, 20%; DDSA/AFU molar ratio of 0.15; time, 1 h; temperature, 25 °C. 0.1 DTAB/AFU molar ratio.
[a] DS by NMR method, average of three experiments.

2.6. Reaction efficiency

In order to measure the effectiveness of the system during the hydrophobic modification of inulin with ASA, reaction efficiency (RE) was calculated by dividing the estimated DS of the end-product by the theoretical DS according to the amount of ASA added to the reaction crude. The theoretical DS was calculated assuming that all of the added anhydride reacted with inulin to form ester derivative. The RE was calculated as follows:

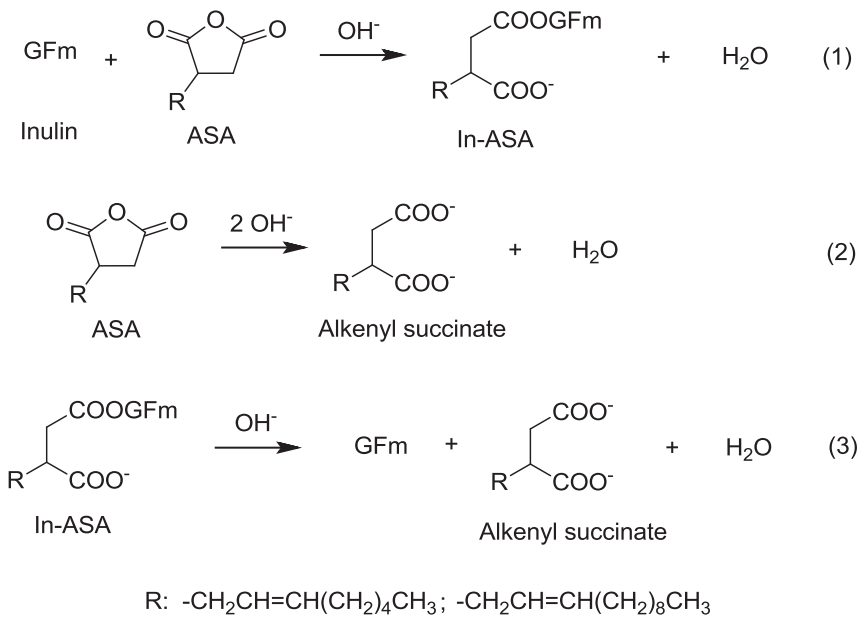
$$\mathrm{RE}(\%) = \frac{\text{actual DS}}{\text{theoretical DS}} \times 100$$

3. Results and discussion

For the starting conditions, we used experimental conditions described by other authors for the synthesis of ASA modification of starch in aqueous slurry systems (Chi et al., 2007; Jeon, Viswanathan, & Gross, 1999; Song, He, Ruan, & Chen, 2006).

In this work, In-ASA modifications were carried out by the base catalyzed addition of ASA to an inulin–water system. In order to modify inulin with ASA anhydrides efficiently we studied the effect of inulin concentration, pH range, reaction temperature and length of the alkenylsuccinic anhydrides. Both OSA and DDSA were not fully soluble in the aqueous medium. This solubility was related to the chain length of ASA. Consequently, while In-OSA could be obtained in water media, In-DDSA might need the presence of DTAB micelles to solubilise DDSA. Thus, the effect of the addition of a cationic surfactant such as DTAB was evaluated to prepare In-DDSA modified inulin.

Esterification of inulin occurred by nucleophilic substitution reaction between the ionized hydroxyl groups of inulin and the hydrophobic anhydride. Scheme 1 shows the chemical reactions occurring during the inulin esterification with alkenyl succinic anhydrides in presence of an aqueous basic solution. The base is used to enhance the nucleophilicity of the hydroxyl groups of GF_m (inulin) and also to swell its globular aggregates (Morros et al., 2010a). In consequence, the alkenyl succinic anhydrides can react with GF_m resulting in alkenyl succinates of inulin (reaction 1, Scheme 1). However, 2 equivalents of sodium hydroxide also

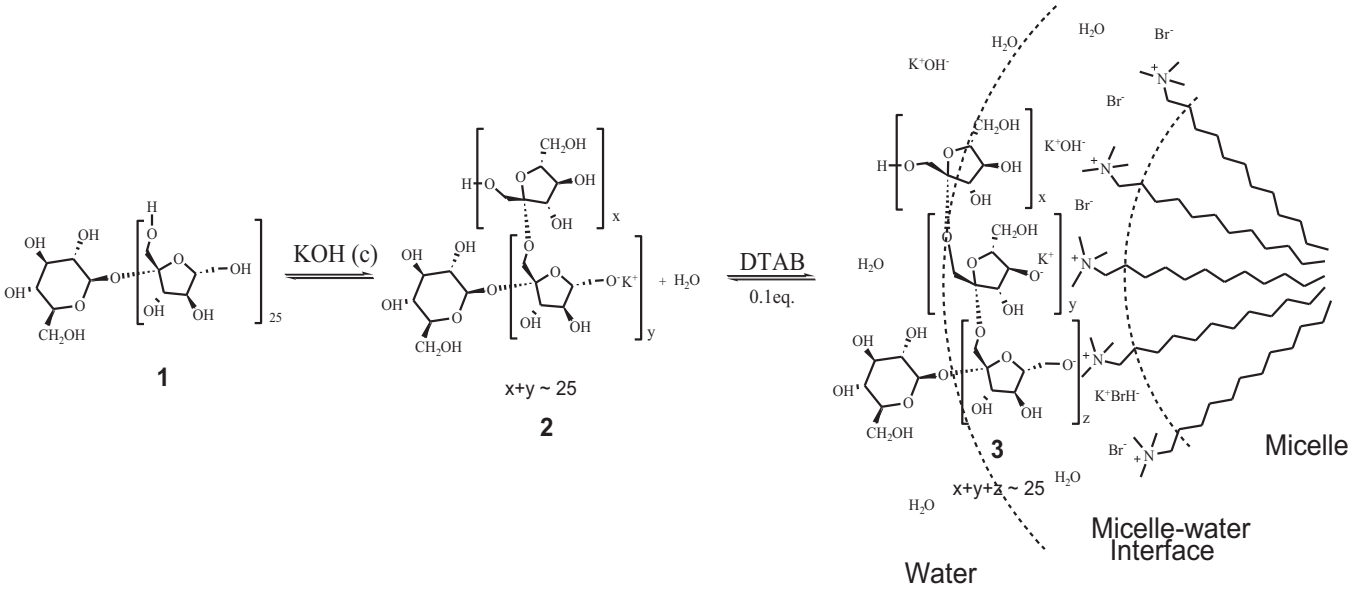


Scheme 1. Chemical reactions during hydrophobic modification in aqueous media: (1) In-ASA esterification, (2) ASA hydrolysis, and (3) In-ASA hydrolysis.

produced the hydrolysis by-product such as alkenyl succinate salt formed from the anhydride (reaction 2, Scheme 1) and/or from the inulin ester (reaction 3, Scheme 1) (Dan et al., 2009). Under these conditions, it is important to consider that hydrolysis and esterification are competitive reactions. Following the reactions of Scheme 1, the reactive ASA species could react with inulin to yield In-ASA ester molecules or could be hydrolyzed forming salts of alkenyl succinate. These two reactions produced a pH decrease. Therefore, the reactions were conducted at pH range between 8.0 and 9.5, and the end of the reaction was established when the pH was kept constant during more than 1 h.

Scheme 2 shows the aqueous dynamic equilibrium of inulin in presence of a base and DTAB cationic surfactant. A similar mechanism was also proposed for the synthesis of long chain inulin β-hydroxyalkyl ethers in presence of DTAB (Morros et al., 2010b). The solubilised inulin (1) in the presence of potassium hydroxide (KOH) is converted into a more reactive form with its hydroxyls ionized (2) through a normal acid–base equilibrium. Negatively charged inulin (2) is bounded mainly by electrostatic interactions to the DTAB micelle–water interface (3) characterized to have a multiplicity of positive charges. At this region, the nucleophilic reactivity of inulin could be increased not only for the extent of the ionization produced by KOH, but also for the degree of association with DTAB molecules.

At this point, because of the minor stability of ester bonds in high alkaline aqueous media, the pH should be adjusted between 8 and 9. Under these pH conditions, inulin would precipitate like in neutral aqueous solution, but we can expect that thanks to the inulin–DTAB complex the precipitation will be prevented. Then the displacement of K^+ and the solvation water molecules to outer regions provoked by the interaction between the DTAB and inulin should provide an enhanced environment to the desired O-ring opening ASA reaction, minimizing side reactions such as reaction 2 or 3.



Scheme 2. Schematic representation of the aqueous dynamic equilibrium of inulin in presence of a base and a cationic surfactant (before adding the ASA).

Our discussion in terms of consistency of the model proposed before with the observed results or not, is presented.

3.1. In-OSA modification in water

3.1.1. Effect of inulin concentration

Details of the synthesis and reaction efficiencies for In-OSA in water at 35% (w/w) inulin (reaction 1, Table 1) and 20% (w/w) inulin (reaction 3, Table 1) are shown in Table 1. For both reactions pH range was kept between 8.5 and 9.0. The RE for reaction 1 was 56 ± 38% and the RE for reaction 3 was 88 ± 5%. As expected, higher RE values with a good reproducibility were obtained for 20% (w/w) inulin concentration. Therefore, a 20% (w/w) concentration of inulin will be used for subsequent experiments.

Hydrophobic In-ASA modification in aqueous alkaline suspension was a heterogeneous reaction media. It is known that inulin supramolecular aggregates were fairly soluble in water at room temperature (Dan et al., 2009) and formed gel particles at higher concentrations when mixed with water (Bot, Erle, Vreeker, & Agterof, 2004). Moreover ASA species were not fully soluble in water, so the esterification reaction should occur between partially solubilised ASA and the accessible inulin hydroxyls favoring the hydrolysis side reactions. All these facts could explain the lower RE and high variability in DS values at inulin concentrations of 35%.

3.1.2. Effect of pH range

According to Song et al. (2006), an important parameter for the OSA starch modification is the pH of the reaction system. Table 1 shows the RE values obtained for In-OSA reactions carried out at three pH range values: 9.0–9.5 (reaction 2, Table 1), 8.5–9.0 (reaction 3, Table 1) and 8.3–8.5 (reaction 4, Table 1). The rest of parameters were inulin concentration at 20% (w/w), OSA/AFU molar ratio of 0.18 and a reaction temperature of 25 °C.

Results in Table 1 indicate that the RE substantially increases when the pH of the reaction decreases. According to Scheme 1, the hydrolysis reaction needs 2 equiv. of base, while the esterification only needs 1 equiv. of base. Then, we could expect that pH values higher than 9.0 will favor OSA hydrolysis, while pH values between 8.3 and 8.5 favor the esterification of inulin. Concerning the reaction time, lower pH gave longer reaction times, but less hydrolysis by-products.

Interestingly both NMR and titration methods for In-OSA (DS) determination were comparable to each other (see Table 1, reactions 2 and 3). However we rejected titration method due to the large amount of product needed to do the analysis. Even so, it could be useful for large scale productions.

3.2. In-DDSA esters of inulin in water–DTAB surfactant media

Esterification of inulin with DDSA was first tried out in water at an inulin concentration of 20%, pH 8.3–8.5, and at 25 °C. At these conditions a RE of 35% was obtained after a very long reaction time of 24 h (reaction 5, Table 1) compared with that of In-OSA reaction time of 8 h (reaction 4, Table 1). At this concentration the gelation process of the mixture occurred during the last part of the reaction time and, as we observed using 35% inulin concentration (reaction 1, Table 1), it could have a negative effect on RE and the variability of the estimated DS. At this stage, new experimental conditions in aqueous DTAB-micellar catalysis to obtain In-DDSA esters were investigated. As we described in Scheme 2 the interaction between the cationic polar head of the surfactant on the inulin hydroxyls together the micellar solubilisation of DDSA micelles could improve the reaction efficiency and reaction rate in the same way that the inulin etherification while gelation process is prevented (Morros et al., 2010b).

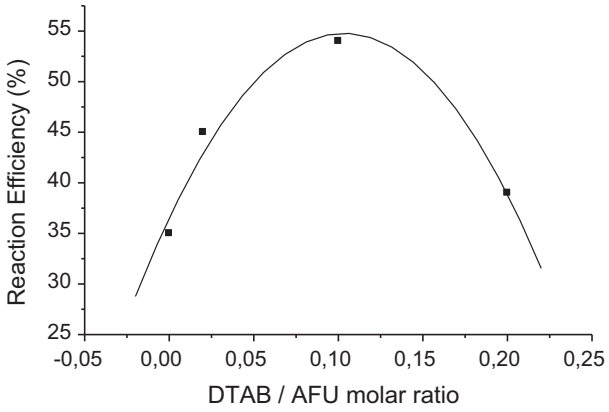


Fig. 3. Effect of DTAB/AFU molar ratio on In-DDSA reaction efficiency. Reaction conditions: inulin concentration, 20%; DDSA/AFU molar ratio of 0.15; time, 1 h; pH range, 8.5–9.0; temperature, 25 °C.

3.2.1. Effect of pH range

Given that the In-ASA reaction is dependent on the pH range, we first studied the optimal pH range in the In-DDSA esterification in presence of DTAB. Taking into account our results from the synthesis of β-hydroxyalkyl ethers of inulin in water–DTAB media (Morros et al., 2010b), the synthesis of In-DDSA was first carried out at a 0.1 DTAB/AFU molar ratio surfactant. The reaction media was a single-phase system and the reaction was conducted under gentle stirring.

Results in Table 2 indicate the influence of pH range on In-DDSA modification in water–DTAB system. RE values for In-DDSA depends on the pH range as we observed in In-OSA. In general, the efficiencies were lower than those of In-OSA reactions in water and the optimum pH range was shifted to higher values between 8.5 and 9.0. Comparing this pH range with the optimal pH range found by other authors working in DDSA modification of starch in water, there is no difference between the use of inulin or starch (Jeon et al., 1999). This could mean that, the pH range depends essentially on the chain length of the ASA species. At higher pH range, the swelling of inulin is also higher, reducing the steric hindrance provoked by the bulky chain of DDSA.

3.2.2. Influence of DTAB/AFU molar ratio

Fig. 3 shows the influence of the variation of DTAB/AFU molar ratio on the RE values for In-DDSA esterification reaction at 25 °C for a constant inulin and DDSA concentration. From 0 to 0.1 DTAB/AFU molar ratio, the RE was raised from 35% to 54%. An increase from 0.1 to 0.2 DTAB/AFU molar ratio diminished RE values to 40%.

In the range of DTAB concentrations studied, the best DTAB/AFU molar ratio was 0.1. Interestingly, Durand (2006) and Morros et al. (2010b) reported the same 0.1 DTAB/AFU molar ratio for the best reaction efficiency in β-hydroxydodecyl ethers of dextran and inulin synthesis, respectively. Concerning the reaction time, it is noticeable that in water–DTAB system it decreased significantly. The reaction time was around 24 h in the absence of DTAB but it went down to less than 1 h for 0.2 DTAB/AFU molar ratio. The remarkable increase in reaction rate results from localized concentration and great proximity of both lipophilic and hydrophilic reactants by micellar solubilisation and electrostatic interaction (Scheme 2) (Tascioglu, 1996).

In this micellar DTAB–inulin complex system, esterification and hydrolysis are competitive reactions and both are catalyzed by cationic DTAB micelle interface, see Fig. 4. The variations of RE in Fig. 3 could be a consequence of variations of the electrostatic interactions between DTAB and ionized inulin (inulin + KOH), which were mainly governed by DTAB/AFU ratio. At DTAB/AFU molar

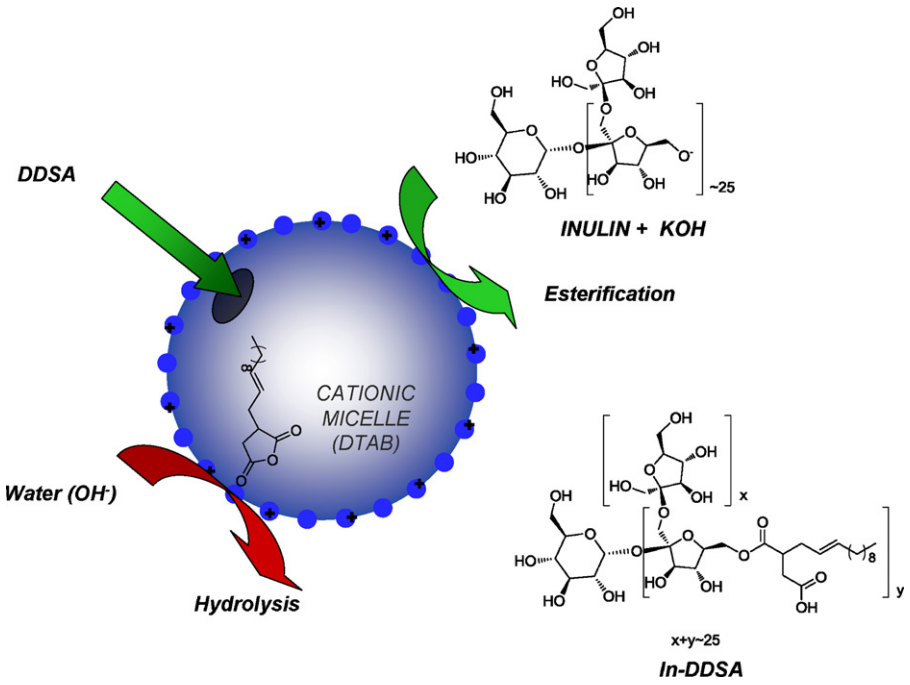


Fig. 4. Schematic representation of the chemical reactions catalyzed by DTAB micelle–water interface during the preparation of In-DDSA derivative.

ratio < 0.1, the increase in RE with DTAB could be explained by a major acceleration of the esterification reaction with respect to hydrolysis, since inulin tends to be adsorbed to the DTAB micelles interface provoking the displacement of water molecules from there to the bulk phase.

At 0.1 DTAB/AFU molar ratio, the RE value obtained is around 50%, the increase of cationic micelle interface due to the higher DTAB concentration (Hayter & Penfold, 1983) could let the inulin chains in the bulk phase to cover all available micelles interface, reaching the highest esterification rate for the system. At higher DTAB concentration, 0.2 DTAB/AFU molar ratio, the higher amount of micelles could increase the hydrolysis rate instead of the esterification. This could happen because the newly formed micelles could have less inulin at their surface, having more free reactive points available for the water molecules and therefore for hydrolysis.

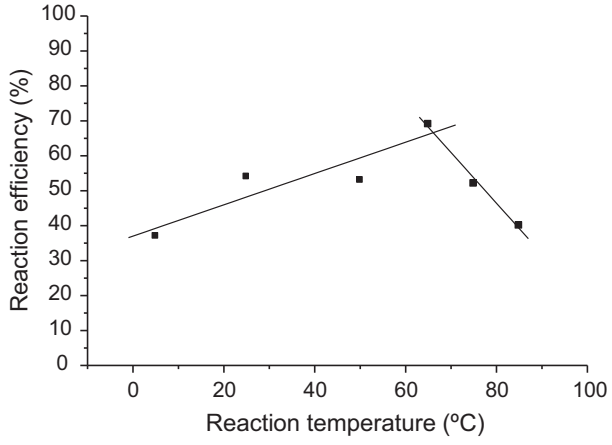


Fig. 5. RE for the DDSA–inulin modification in DTAB–H_2O system at different reaction temperatures. Reaction conditions: inulin concentration, 20%; time, 1 h; pH range, 8.5–9.0; DS by NMR method, average of three experiments with 10% of fault. The straight black lines represent the tendency of the system to esterify inulin (from 5 °C to 65 °C) and to hydrolyze ester bonds (from 65 °C to 85 °C) when the reaction temperature is increased.

3.2.3. Temperature effect

At this point, all experiments described above were carried out at 25 °C. The effect of reaction temperature on reaction efficiency was studied at temperatures between 5 °C and 85 °C. The reaction conditions were 20% of inulin concentration, DDSA/AFU molar ratio of 0.15, 0.1 DTAB/AFU molar ratio and pH range 8.5–9.0. Fig. 5 shows how RE was affected by reaction temperature. As expected increasing the temperatures from 5 °C to 65 °C the RE increased from 37% to values near 70%. At temperatures higher than 65 °C, the RE decreased with the temperature until values around 40%. The decreasing of the RE could be associated to the hydrolysis of the ester bond that is favored by the higher solubility of In-DDSA in the bulk water phase. The relative magnitude of these two opposing effects, therefore, determines whether the RE value increase or decrease over a particular temperature range.

4. Conclusions

Inulin-based surfactants by reaction of octenyl succinic anhydrides (OSA) and dodecenyl succinic anhydrides (DDSA) with inulin in aqueous media were prepared. Optimal conditions for In-OSA and In-DDSA were investigated. The most favourable water reaction media depended on the length of ASA. In-OSA was obtained in pure water at pH 8.3–8.5 with a RE of 94% in 8 h, while In-DDSA was synthesized in DTAB–water media at pH 8.5–9.0 with RE of 54% in 1 h. In this micellar DTAB–inulin–water complex system, esterification and hydrolysis are competitive reactions catalyzed by cationic DTAB micelles being the DTAB/AFU molar ratio and temperature two parameters that can influence strongly on the RE of the In-DDSA reaction. The aim of this study was to indicate the role of DTAB in promoting the ASA esterification of inulin. Even though we have tried to give an explanation for the experimental results, a more precise study including techniques like TEM/SEM, DLS, etc. to show the proper picture of the complex particularly in DTAB–inulin systems would be necessary to understand this micellar catalytic system.

Acknowledgments

The authors gratefully acknowledge financial support from ORAFTI Bio Based Chemicals and from the Spanish Ministry of Science and Education (CTQ2009-14151-C02-01 grant).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carbpol.2010.12.077.

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