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Chemical hydrophobic modification of inulin in aqueous media: Synthesis of β-hydroxyalkyl ethers of inulin

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ABSTRACT

Neutral hydrophobic β-hydroxyalkyl ethers of inulin have been prepared with varying molecular features (the hydrophobic characteristics of the epoxide, length and nature, and the number of grafted groups per fructose units) in aqueous media under different conditions. The influence of several reaction parameters such as amount of solubilizer (isopropyl alcohol), basic catalysts, reaction time and temperature on the reaction efficiency has been studied through NMR analysis. We can state that the etherification of inulin in water is limited by the hydrophobic effect due to the alkyl chain of the epoxide, which can be avoided by adjusting the required amount of a solubilizer. On the other hand, the etherification rate appears to be strongly related to the temperature. Pure short and medium chain length β-hydroxyalkyl ethers of inulin can be obtained in KOH water media at 80 °C using 40% (w/w) of inulin concentration with reasonably good efficiencies and reaction times.

1. Introduction

Society is progressively more worried about safety issues while working for a sustainable future. Sustainable chemistry represents an area of innovation, which not only preserves resources, but stands for a development process in the chemical industry. The most important goals in the advance of fine chemicals, skin care, and pharmaceutical products including biomedical compositions are the development of non-toxic and biodegradable compounds, the advances on new reaction conditions (cleaner solvents, biotechnological processes) and the use of raw materials as renewable feedstock (Vemula & John, 2008).

Polymeric surfactants are an important class of chemicals involved in many colloidal dispersed systems as stabilizers for oil in water emulsions, or solid in liquid dispersions, and for the control of surface characteristics of particles among others. For this reason, they are broadly applied in food, cosmetics and pharmaceuticals (Garnier, Laschecksky, & Storsberg, 2006).

Hydrophobically modified water-soluble polymeric surfactants derived of natural polysaccharides like cellulose (Landoll, 1982), starch (Wesslén & Wesslén, 2002), dextran (Rouzes, Durand, Leonard, & Dellacherie, 2002), chitosan (Desbrières, Martinez, & Rinaudo, 1996), and inulin (Stevens, Meriggi, & Booten, 2001; Stevens, Meriggi, Peristeropoulou, et al., 2001) are attractive amphiphilic polymers of increasing interest due to their additional sustainable properties such as low toxicity and biodegradability (Scott & Jones, 2000).

Inulin, a product extracted from tubers and roots of plants such as *Cichorium intybus* (Chicory), *Helianthus tuberosus* (Jerusalem artichoke) and *Dahlia*, belongs to the second most important group of polysaccharides called fructans. Inulin (GF_n) consists mainly of polydisperse linear β (2 → 1) linked polyfructose (F) with average length of 25 (*n*) and typically has a terminal glucose unit (G). Fig. 1 illustrates the structure of inulin elucidated by De Bruyn, Alvarez, Sandra, and Leenheer (1992).

Many efforts have recently been devoted to the chemical modification of inulin in order to develop industrial products with specific characteristics (Stevens, Meriggi, Peristeropoulou, et al., 2001). Several amphiphilic polymers obtained from inulin have been prepared by esterification (Rogge & Stevens, 2004), etherification (Rogge et al., 2004) and carbamoylation (Stevens, Meriggi, & Booten, 2001; Stevens, Meriggi, Peristeropoulou, et al., 2001) of inulin using fatty acid methyl esters (FAME), alkyl epoxides, and alkyl isocyanates, respectively. A commercial example is INUTEC® SP1, a non-ionic polymeric-based surfactant, derived from carbamoylation of chicory inulin which is used as an emulsion stabilizer for o/w emulsions (Tadros, 2009). Compared to esters or carbamates, ethers are more resistant to cleavage by acids, alkali and mild oxidizing agents, which can be used as an advantage to extend their field of application.

Most inulin-based surfactants are chemically synthesized in anhydrous organic solvents which can dissolve both inulin and the

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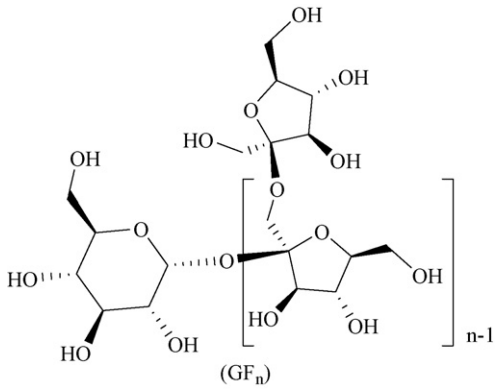


Fig. 1. Main chemical structure of inulin (GF$_n$). *n* corresponds to the degree of polymerization of β-D-fructofuranose units (anhydrous fructose units, AFU).

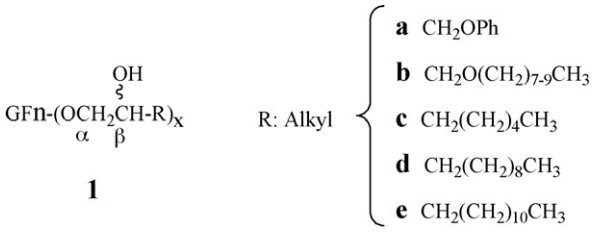


Fig. 2. Structure of β-hydroxyalkyl ethers of inulin synthetized: β-hydroxy-3-phenoxypropyl ether (1a), β-hydroxy-3-oct/decoxypropyl ether (1b), β-hydroxyoctyl ether (1c), β-hydroxydodecyl ether (1d), β-hydroxytetradecyl ether (1e). *X* corresponds to the number of grafted groups per fructose unit.

hydrophobic reactant. Because of the absence of water in the reaction medium, these modifications give mainly the desired products without reactant hydrolysis by-products. There are many potential advantages of replacing organic solvents with water; the most obvious are the following: cost, operational simplicity and environmental safety.

The aim of this work was to prepare neutral hydrophobic β-hydroxyalkyl ethers of inulin in aqueous media (Fig. 2) with varying molecular features (the hydrophobic characteristics of the epoxide, length and nature, and the number of grafted groups per fructose units).

The etherification of inulin in aqueous basic solution was described for the first time in the early twentieth century by Tomecko and Adams (1923) and later by Schacht, Ruys, Vermeersch, and Remon, 1984 using allyl bromide and epichlorhydrin, respectively. The work of Kunz and Haji (1995) reported the etherification of inulin with alkylepoxides. However, this last method is limited to water-soluble alkyl epoxides such as ethylene and propylene oxide with reaction efficiencies above 70%. Less soluble epoxides such as butyl epoxide or 1,2-hexyl epoxide gave reaction efficiencies no higher than 40%.

The proposed compounds of Fig. 2 were prepared by O-covalent attachment of 1,2-alkyl epoxides onto the polysaccharide backbone of inulin using homogeneous basic catalyst systems, preferably in water. The design of the chemical process was based on the study of the influence on reaction efficiency of several reaction parameters such as type of catalyst, temperature, base concentration, inulin concentration, epoxide hydrophobicity, and the presence of a co-solvent in the reaction media, estimated by ^{1}H NMR analysis of the pure end product.

Fig. 3 shows that the chemical reactions occurred during the inulin etherification with alkyl epoxides. It is well known that the base acts as activating agent of hydroxyl groups that can react with the epoxide by an O-ring opening reaction. Thus, in the presence of a base, the 1,2-alkylepoxide reacts with GF$_n$OH resulting in β-hydroxyalkyl ether (reaction 1). In the presence of water, the epoxide can also be hydrolyzed giving the undesired 1,2-glycols (reaction 2) that, at the same time, can be activated by the base to react with another epoxide molecule giving oligomeric glycols (reaction 3).

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. It was dried at 70 °C during 24 h before use. The following 1,2-alkylepoxides were used for the hydrophobic modification of inulin: 1,2-epoxy-3-phenoxy propane (or phenyl glycidyl ether) and 1,2-epoxy-3-oct/decoxy propane (or octyl/decyl glycidyl ether) +80% of purity (Technical Grade), 1,2-epoxyoctane, 1,2-epoxydodecane and 1,2-epoxytetradecane +95% of purity. All of them were supplied from Aldrich (St. Quentin Fallavier, France). N-methylpyrrolidone (NMP) was supplied by ORAFTI Bio Based Chemicals (Tienen, Belgium) at present BENEO-BBC), tetrabutylammonium hydroxide 1 M aqueous solution (TBAOH) from Aldrich and isopropyl alcohol (IPA) supplied by Carlo Erba 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, capacity of approximately 100 mL/ft, and a pore size of 2000 NMWCO was used. Bulk ethanol (96%) used

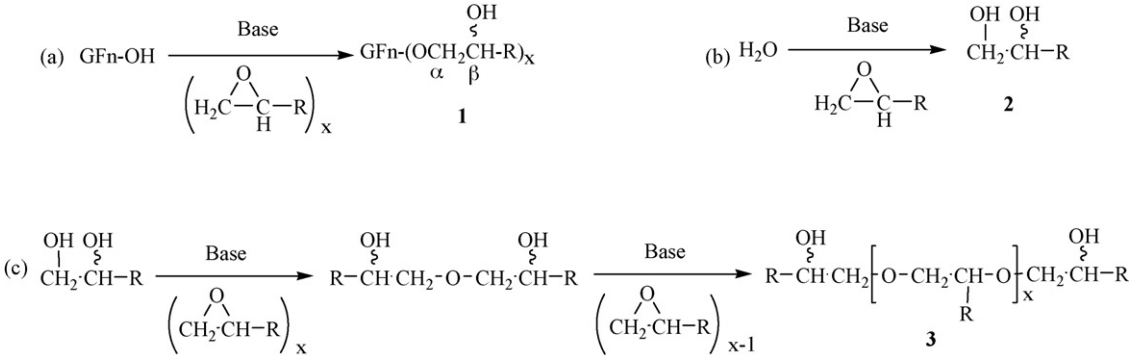


Fig. 3. Chemical reactions during the etherification of inulin in water: (a) etherification: formation of β-hydroxyalkyl ether (1); (b) epoxide hydrolysis: formation of 1,2-glycols (2); (c) oligomerization: formation of oligomeric glycols (3).

Table 1
Synthesis of β-hydroxydodecyl ether of inulin(1d) in anhydrous NMP at 80 °C using different catalysts.

Reaction no.	Basic catalyst	Molar ratio catalyst/AFU[a]	Time (h)	Efficiency (%)[b]
1	$NaHCO_3$ + LiCl	0.01 + 0.1	3	7
2	Li_2CO_3	0.01	3	1
3	NaH	0.01	3	1
4	DMAP	0.01	3	2
5	Et_3N	0.01	3	2
6	Et_3N	0.1	3	3
7	Et_3N + DMAP	0.01 + 0.01	3	4
8	Et_3N + DMAP	0.01 + 0.01	72	28
9	Et_3N + LiCl	0.01 + 0.1	3	1

[a] Epoxide/AFU molar ratios between 0.1 and 0.3.
[b] Average of three experiments.

for purification through dialysis was supplied by the Chemical Department Store of CSIC (Barcelona, Spain). Acetone, methanol and dichloromethane for crystallizations and washes were supplied by Merck (Darmstadt, Germany) in a SupraSolv grade.

2.2. Analytical methods

TLC (Thin Layer Chromatography) was used to determine the free amount of unreacted epoxide using Alugram® Nano – SILG/UV_{254} as a layer, ethyl acetate/hexane (1/4) as a mobile phase and 5% phosphomolybdic acid/ethanol solution as a revealer at 100 °C. HPLC (high performance liquid chromatography) was used as well to confirm the absence of free epoxide in the final β-hydroxyalkyl ethers of inulin powder, using Licrospher 100 CN (5 μm) column, ACN/water (2/3) mobile phase, Merck-Hitachi L6200 pump and a UV or RI detector. ^1H 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, with 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. 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. Synthesis of β-hydroxyalkyl ether of inulin in different catalyst systems

2.3.1. Preparation of β-hydroxydodecyl ether of inulin(1d) in NMP as solvent with different basic catalysts

5 g of inulin (31 mmol of anhydrous fructose units, AFU) were dissolved in 20 mL NMP at 50 °C. The 20% (w/w) solution of inulin in NMP was evaporated under high vacuum up to a 40% (w/w) solution in order to remove the water that is present in the inulin–NMP system. The anhydrous solution was brought into a 100 mL three-neck round-bottom flask and the corresponding amount of the basic catalyst was added. Oxygen was removed by flushing with nitrogen gas. The reaction media was stirred at 80 °C for 1 h and 1,2-epoxydodecane was added gradually, between 0.05 and 0.3 epoxide/AFU molar ratios, to the reaction mixture during approximately 1 h. After a reaction time of several hours, the reaction crude brown syrup was cooled to room temperature and poured into dry acetone under vigorous stirring. 1d crystallized immediately and was filtered over a sintered glass filter. The modified inulin was washed with dichloromethane to remove the NMP. The resulting powder was dried under high vacuum to give 1d with 85–90% of average yield after crystallization. Details of the synthesis and reaction efficiencies are depicted in Table 1.

2.3.2. Preparation of β-hydroxydodecyl and β-hydroxytetradecyl ethers of inulin(1d and 1e, respectively) in water–NMP (1:1) mixtures with different basic catalysts

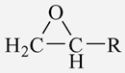
1 g of inulin (6.2 mmol of AFU) was dissolved in 5 mL NMP at 50 °C. The 17% (w/w) solution of inulin in NMP was brought into a 25 mL round-bottom flask and the corresponding amount of catalyst dissolved in 5 mL of water was added. The reaction media was stirred at reaction temperature for 1 h and the 1,2-epoxydodecane or 1,2-epoxytetradecane was added gradually, between 0.05 and 0.3 epoxide/AFU molar ratios, during approximately 1 h. Once the reaction concluded, the crude was cooled to room temperature and neutralized with HCl 5% to a pH of 6.00. The reaction mixture was dialyzed against water, 50% ethanol/water and ethanol (abs). The resulting suspension was then poured into dry acetone under vigorous stirring. 1d and 1e crystallized immediately and were filtered over a sintered glass filter. The resulting powder was dried under high vacuum to give 1d and 1e with 70% of average yield. Details of the synthesis and reaction efficiencies are depicted in Table 2.

Table 2
Synthesis of β-hydroxydodecyl ether of inulin in water–NMP (1:1) mixtures using different catalysts.

Reaction no.	Basic catalyst	Molar ratio catalyst/AFU[a]	Temperature (°C)	Time (h)	Efficiency (%)[b]
10	–	0	80	18	0
11	KOH	0.1	80	18	0
12	KOH	0.2	80	18	0
13	KOH	0.4	80	18	22
14	KOH	0.6	80	18	16
15	KOH	1.0	80	18	9
16	DABCO	0.1	80	18	1
17	DMAP	0.1	80	18	5
18	Et3N	0.1	80	18	2
19	TBAOH	0.8	80	18	23
20	TBAOH	0.8	r.t	120	96
21	TBAOH	0.8	r.t	168	56[c]

[a] Epoxide/AFU molar ratios between 0.1 and 0.3; inulin concentration: 10% (w/w).
[b] Average of three experiments.
[c] Synthesis of β-hydroxytetradecyl ether of inulin(1e).

Table 3
Synthesis of various β-hydroxyalkyl ethers of inulin in water using KOH[a].

Reaction no.		Solubility in water	Time (h)	Efficiency (%)
22	CH_2OPh	+	3	79
23	$CH_2(CH_2)_4CH_3$	±	14	60
24	$CH_2O(CH_2)_{7-9}CH_3$	–	12	9
25	$CH_2(CH_2)_8CH_3$	–	24	3

Inulin concentration: 40% (w/w). KOH/U molar ratio: 0.4; $NaBH_4$/AFU molar ratio: 0.01; reaction temperature: 80 °C.
[a] Epoxide/AFU molar ratio between 0.1 and 0.3.

2.3.3. Synthesis of β-hydroxyalkyl ethers of inulin 1(a–d) in water with KOH as a basic catalyst

4 g of inulin (24.7 mmol of AFU) were dissolved in 6.0 mL aqueous solution of 0.6 g KOH (9.1 mmol; 0.37 equiv. based on AFU) and 0.010 g $NaBH_4$ (0.3 mmol; 0.01 equiv. based on AFU) under vigorous stirring at 25 °C. The 40% (w/w) solution of inulin was brought into a 25 mL round-bottom flask. The reactor was then heated to 80 °C. After stirring for 1 h, the corresponding amount of 1,2-alkyl epoxide was added gradually, between 0.05 and 0.3 epoxide/AFU molar ratios, during approximately 1 h. After a reaction time of several hours, the reaction mixture was cooled to room temperature and neutralized with HCl 5% to a pH of 6.00. After that, it was dialyzed against water, ethanol/water (1/1) and ethanol (abs). The resulting suspension was then poured into dry acetone under vigorous stirring. The β-hydroxydodecyl ether of inulin 1(a–d) crystallized immediately and was filtered over a sintered glass filter. The resulting powder was dried under high vacuum to give 1(a–d) with an average yield of 70%. Details of the synthesis and reaction efficiencies are depicted in Table 3 and Fig. 5.

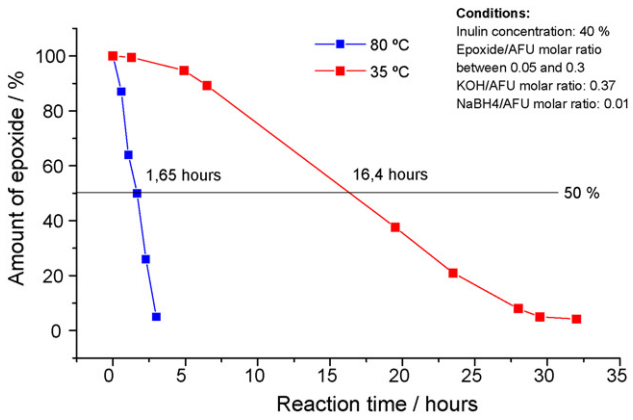


Fig. 5. Influence of reaction temperature on the etherification of inulin with phenyl glycidyl ether.

2.3.4. Preparation of various β-hydroxyalkyl ethers of inulin 1(b–d) with KOH as a basic catalyst in water–IPA mixtures

4 g of inulin (24.7 mmol of AFU) were dissolved in 6 mL aqueous solution of 0.6 g KOH 85% of purity (9.1 mmol; 0.37 equiv. based on AFU) and 0.010 g $NaBH_4$ (0.3 mmol; 0.01 equiv. based on AFU) under vigorous stirring at 25 °C. The 40% (w/w) solution of inulin was brought into a 25 mL round-bottom flask. The reactor was heated to 80 °C and after stirring for 1 h, a solution of the corresponding amount of 1,2-alkyl epoxide, between 0.05 and 0.3 epoxide/AFU molar ratios, dissolved in the required amount of IPA (isopropanol) was added gradually to the reaction mixture during approximately 1 h. The mixture was cooled to room temperature and neutralized with 5% HCl to a pH of 6.00. Then, it was dialyzed against water, ethanol/water (1/1) and, ethanol (abs). The resulting suspension was poured into dry acetone under vigorous stirring. The β-hydroxydodecyl ether of inulin 1(b–d) crystallized immediately and was filtered over a sintered glass filter. The resulting powder was dried under high vacuum to give 1(b–d) with an average yield of 70%. Details of the synthesis and reaction efficiencies are depicted in Fig. 6.

2.4. Product characterization

The characterization of β-hydroxyalkyl ethers of inulin was performed on the basis of their degree of substitution (DS) which is defined by the number of alkyl chains per fructose units. After purification of the end products, the DS was estimated from a comparative analysis of ^{1}H NMR signals (500 MHz, 30 mg mL^{-1} in DMSO-d_6, 50 °C) of the alkyl chains and fructose units with less than a 10% of fault (Rogge & Stevens, 2004). The etherification of modified inulin was also confirmed using ^{13}C NMR and FT-IR spectroscopy.

In order to measure the effectiveness of the catalyst system in the hydrophobic modification of inulin with different 1,2-alkyl epoxides, reaction efficiency (RE) was calculated by dividing the estimated DS of the end product by the theoretical DS according to the amount of epoxide added to the reaction crude. See Fig. 4.

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

Fig. 4. Equation of reaction efficiency (RE).

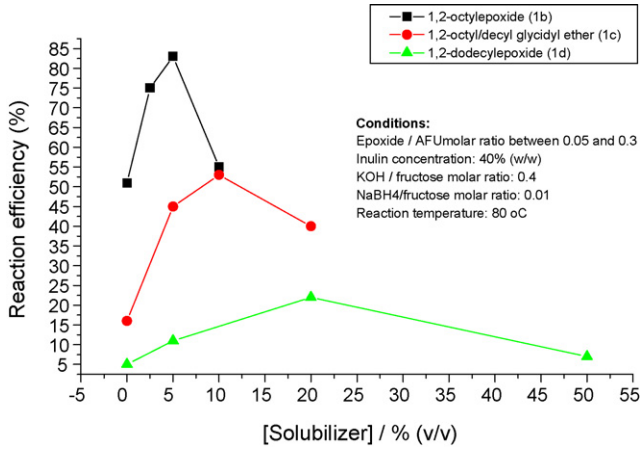


Fig. 6. Etherification of inulin with different alkylepoxides as a function of IPA (solubilizer) concentration in water.

3. Results and discussion

3.1. Synthesis of the β-hydroxydodecyl ether of inulin(1d) in anhydrous NMP at 80 °C using different catalysts

3.1.1. Type of catalyst effect

The synthesis of the β-hydroxydodecyl ether of inulin was first carried out by using the quantitative method to prepare alkyl inulin ethers with propylene oxide, in NMP organic solvent using Et_3N as organic base (Rogge et al., 2004), but very low efficiency was obtained. NMP was selected as the organic solvent because both inulin and 1,2-dodecylepoxide were soluble. Consequently, the reaction media was homogeneous.

Because of the low reaction efficiency, a suitable range of basic inorganic and organic catalysts, some already used for alkoxylation of polysaccharides (Gagnaire, Toraman, Descotes, Bouchu, & Queneau, 1999; Wesslén & Wesslén, 2002), have been evaluated. However, under these conditions, the type and amount of basic catalyst were not high enough to achieve a sufficient activation of inulin. Table 1 shows that reaction efficiencies with different types and amount of catalysts were very low. Even with reaction times of 72 h, the efficiency was as low as 28%. While short chain epoxides (ethylene oxide or propylene oxide) gave almost quantitative yields of inulin modification in these conditions (Rogge et al., 2004), inulin practically remained unaltered in presence of 1,2-dodecylepoxide.

3.2. Synthesis of β-hydroxydodecyl ether of inulin in water–NMP (1:1) mixtures with different catalysts

3.2.1. Amount of catalyst effect

Because of the poor reactivity of inulin against 1,2-dodecylepoxide using NMP, our efforts were focused to increase the amount of catalyst in the media. To do that, water–NMP (1:1) mixtures were used in the synthesis of β-hydroxydodecyl ether of inulin. Most of the ionic inorganic catalysts used in NMP media were insoluble over 2% (w/w), but its solubility increased by the addition of water into the media. The solubility of non-ionic organic catalysts (i.e. DMAP) was 20% (w/w) in water–NMP (1:1) mixtures. Ionic organic catalyst such as tetraalkylammonium hydroxide (TBAOH) was solubilized completely in a wide range of NMP/water mixtures (Durand & Dellacherie, 2006). The epoxide was still soluble despite the presence of water and 10% of inulin concentration was used. The efficiencies of the reaction in these conditions are shown in Table 2.

No significant effect of the base concentration is evidenced increasing the amount of catalyst in water–NMP media at 80 °C (Table 2, entries 10–19), although a maximum efficiency of 22% was achieved at 0.4 molar ratio KOH/fructose at this temperature. At higher catalyst concentrations and at 80 °C the presence of water produced the epoxide hydrolysis (Table 2, entries 14 and 15, Fig. 3b) with subsequent formation of glycols. A considerable increase of the reaction efficiency was observed when TBAOH was used as catalyst at room temperature in a NMP–water (1:1) media, but similar low efficiencies were obtained at 80 °C due to epoxide hydrolysis. However, in the case of β-hydroxydodecyl and β-hydroxytetradecyl ether (entries 20 and 21), a good efficiency required a long reaction time and a very high catalyst/fructose-ratio with limited practical uses.

3.3. Synthesis of various β-hydroxyalkyl ethers of inulin in water using KOH as a basic catalyst

Taking into account that ionic basic catalysts, KOH and TBAOH, turned out to be the most appropriate for the β-hydroxyalkoxylation of inulin in water–NMP (1:1) media (see Table 2), the etherification reactions in water were carried out with 5% (w/w) KOH (molar ratio catalyst/fructose of 0.37) as a catalyst. Surprisingly under these conditions, inulin could be concentrated until 40% (w/w) at room temperature. Several parameters such as temperature, hydrophobic features of alkylepoxides and presence of isopropanol (IPA) as a solubilizer on the reaction efficiency were examined.

3.3.1. Temperature effect

Temperature effect was evaluated on the basis of the etherification with a soluble epoxide (phenyl glycidyl ether). Fig. 5 shows the evolution of the phenyl glycidyl ether concentration in the reaction mixture during the reaction time at two different temperatures. Increasing the reaction temperature from 35 to 80 °C resulted in a 10-fold increase in the rates of epoxide consumption, the RE at 80 °C being 85% while RE at 35 °C being 67%. These experimental data demonstrate that temperature plays an important role accelerating the etherification of inulin carried out with phenyl glycidyl ether. The reason for this could be found in the particular hydrophilic backbone of inulin that forms intra and intermolecular hydrogen bonds. The steric hindrance due to the hydrogen bonding could be affected by temperature, allowing the hydroxyl groups react more easily. However, dark-brown coloration (probably due to an oxidation process) took place at 40% (w/w) inulin water solution which can be avoided adding 0.1% (w/w) of $NaBH_4$ to the reaction mixture (BeMiller, Steinheimer, & Allen, 1967).

3.3.2. Solubility–reactivity relationship

The relationship between the solubility and the reactivity of the 1,2-alkyl epoxides against inulin was studied in water media. Table 3 shows that in general, a decrease of the solubility in water gives a decrease in the etherification efficiency. The more soluble the alkylepoxide (phenyl glycidyl ether, Table 3, entry 22), the higher its efficacy. Furthermore, comparing reactions 24 and 25, one can note that the presence of an oxygen atom in the position 2 of the epoxide chain accelerates the reaction. This may be due to minor hydrophobic features as a result of the introduction of a heteroatom in the alkyl chain.

3.3.3. Effect of isopropyl alcohol (IPA) as solubilizer

Since the reactivity of the alkyl epoxides and their solubility decreases with hydrophobicity, the efficiency of the reaction can be increased by adjusting the proportion of IPA–water mixtures (Stevens, Meriggi, & Booten, 2001; Stevens, Meriggi, Peristeropoulou, et al., 2001).

The study of the influence of IPA concentration on the etherification reaction efficiency has been carried out using three alkylepoxides with different hydrophobic characteristics. Fig. 6 shows the reaction efficiency of inulin etherification as a function of IPA concentration in water. In all cases, the efficiency increases when IPA concentration increases until a maximum from which it decreases with the amount of IPA. The required quantity of IPA to achieve the maximum efficiency is closely related to the hydrophobicity of the alkyl epoxide. Additionally, the maximum value of reaction efficiency (RE_{max}) for each alkyl epoxide decreases with the alkyl chain length. Thus, the β-hydroxyoctyl ether (1c) was obtained with RE_{max} of 85% with 5% (w/w) of IPA; the β-hydroxy-3-oct/decoxy propyl ether (1b) was obtained with REmax of 52% with 10% (w/w) of IPA and the β-hydroxyododecyl (1d) was obtained with RE_{max} of 20% with 20% (w/w) of IPA. In fact, the optimal amount of IPA to solubilize the whole epoxide depends on the epoxide chain features, in consequence for more soluble epoxides less IPA is required. However, at IPA concentrations above the RE_{max}, other side O-ring opening reactions such as epoxide hydrolysis (H_2O) and/or alcoholysis (IPA) may occur and result in large amounts of glycols and large periods of dialysis.

4. Conclusions

In conclusion, our results indicate that the etherification of inulin could be limited by the steric hindrance of the inulin chain. To initiate the reaction, a temperature of 60 °C or higher, and a high amount of basic catalyst (5% by weight) was required to activate the hydroxyls of inulin. The more soluble the alkylepoxide (phenyl glycidyl ether), the higher its efficacy. For medium chain length β-hydroxyalkyl ethers of inulin, the reaction was limited by the hydrophobic effect due to the alkyl chain. However, the reaction efficiency could be enhanced adding enough amount of IPA in the reaction media. At this stage, new water systems to obtain long chain β-hydroxyalkyl ethers of 12 and 14 carbon atoms should be investigated.

Acknowledgements

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