Synthesis of β-hydroxyalkyl ethers of inulin in aqueous surfactant media

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ABSTRACT

The synthesis of long chain hydrophobic β-hydroxyalkyl ethers of inulin in aqueous surfactant media is described. β-hydroxyalkyl ethers of inulin were obtained in reaction media containing 40% inulin and 1 M KOH at 80 °C. Several parameters such as the amount and structure of two cationic surfactants (dodecyltrimethylammonium bromide (DTAB) and hexadecyltrimethylammonium bromide (CTAB)) and a non-ionic surfactant (β-hydroxydodecyl ether of inulin (EC12)) as well as the amount and epoxide chain length (C6–C18/26) on the reaction efficiency (RE) were examined through NMR analysis.

We can state that the etherification of inulin in aqueous media with 1,2-dodecylepoxide was dependent on the surfactant used. The non-ionic surfactant, EC12, did not have any effect on the etherification reaction. On the contrary, adding a cationic surfactant such as CTAB or DTAB increased the RE significantly. The effect of DTAB micelles on this reaction could be attributed to both electrostatic (inulin/DTAB) and hydrophobic (epoxide/DTAB) interactions. A micellar catalysis mechanism is proposed to explain these interactions. Efficiencies did not increase more than 50% and were not related to variations in the epoxide alkyl chain.

1. Introduction

The preparation of amphiphilic polymers by linkage of a hydrophilic backbone with several hydrophobic chains is a common industrial procedure due to the excellent properties of the resulting hydrophobically modified water-soluble polymeric surfactants. These compounds are an important class of chemicals involved in many colloidal dispersed systems. For this reason, they are broadly applied in food, cosmetics and pharmaceuticals (Durand & Dellacherie, 2006; Garnier, Lascheksky, & Storsberg, 2006).

Because of the interesting technological characteristics of the inulin biopolymer, a number of amphiphilic polymers from inulin were synthesized, both at research and industrial scale, by reacting fatty acid metyl esters, aliphatic epoxides or aliphatic isocyanates using organic solvents as reaction media (Rogge & Stevens, 2004; Rogge et al., 2004; Stevens, Meriggi, Peristeropoulou, et al., 2001; Stevens, Meriggi, & Booten, 2001). However, due to their environmental impact the development of alternative reaction media has become of great interest. A development in the use of water as a solvent is still a great challenge for this type of organic reactions in which two chemical species of very different polarity (a hydrophilic polymer and a hydrophobic reactant) should react.

Recently, neutral hydrophobic β-hydroxyalkyl ethers of inulin have been prepared by our group 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. These studies indicate that overall the etherification of inulin requires sufficient amount of basic catalyst to activate the hydroxyls of inulin. Moreover, it was observed that the more soluble the alkylepoxide, the higher its efficacy. For more insoluble alkylepoxide, the reaction was limited by the hydrophobic effect due to the alkyl chain length. The etherification with long chain epoxide (C12 and C14) was very difficult to achieve even in water–isopropyl alcohol (IPA) mixtures (Morros, Levecke, & Infante, 2010) giving very low reaction efficiency (RE).

The catalytic effect of surfactant micelles on a great number of reactions is well known (Durand, 2006; Lipshutz & Ghorai, 2009; Miyagawa, Kupka, & Schumpe, 2005; Otto, Engberts, & Kwak, 1998; Siswanto, Battal, Schuss, & Rathman, 1997). The formation of micelles can provide an environment more favourable to the desired reaction, without the addition of an organic solvent (Tascioglu, 1996). 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.

The multiplicity of positively charged hydrophilic heads of cationic micelles may catalyze the reaction between a nucleophilic anion and a neutral substrate (Bunton, Nome, Quina, & Romsted,

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1991; Menger & Portnoy, 1967). In the present decade, an elegant methodology to prepare hydrophobically modified dextran by micellar catalysis has been reported (Durand, 2006). This work concluded that in presence of base the addition of a cationic surfactant promoted polysaccharide hydrophobic modification with 1,2-epoxydodecane. Motivated by these results and to extend our previous work (Morros et al., 2010), in the present article we have studied the effect of addition of surfactants on the etherification of inulin with long chain epoxides in basic aqueous media. Several parameters such as the amount and the structure of surfactant as well as the amount and the epoxide chain length on the reaction efficiency were examined.

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 (phenyl glycidyl ether), 1,2-epoxyoctane from Aldrich (St. Quentin Fallavier, France) and 1,2-epoxydodecane, 1,2-epoxytetradecane, 1,2-epoxyoctadecane and 1,2-epoxy alkane of C20/C28 carbons +95% of purity from Nitrochemie Aschau Gmbh (Germany). The surfactants used were two cationic surfactants, dodecyltrimethylammonium bromide (DTAB) and hexadecyltrimethylammonium bromide (CTAB) supplied from Aldrich (St. Quentin Fallavier, France) and β-hydroxydodecyl ether of inulin (EC12), a non-ionic surfactant synthesized in our lab (Morros et al., 2010). Other chemicals were used as received without further purification. De-ionized 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. De-ionized water and ethanol (96°) were used for purification through dialysis, supplied by the Chemical Department Store of CSIC (Barcelona, Spain).

2.2. Analytical methods

TLC (thin layer chromatography) was used to determine the free amount of unreacted epoxide. Alugram® Nano - SILG/UV$_{254}$ in ethyl acetate/hexane (1/4) and 5% phosphomolybdic acid in ethanol solution at 100 °C were used. Also, HPLC (high performance liquid chromatography) was used to confirm the absence of free epoxide in the final β-hydroxyalkyl ethers of inulin powder, using a Licrospher 100 CN (5 µm) in ACN/water (2/3) pumped by a Merck-Hitachi L6200 and a UV or refraction index (RI) detector. [1]H and ^{13}C nuclear magnetic resonance (NMR) were 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 β-hydroxyalkyl ether of inulin

4 g of inulin (24.7 mmol Anhydrous Fructose Units, AFU) were dissolved in 6.0 mL aqueous solution of 0.6 g KOH 85% 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 into a 25 mL round-bottom flask. Then, 0.76 g of the surfactant (2.6 mmol; 0.1 equiv. based on AFU) were added. After stirring for 30 min, the corresponding amount of 1,2-alkylepoxide was added dropwise. The solution was heated to 85 °C and it was left several hours. The reaction was finished when the free amount of unreacted epoxide was totally consumed (see analytical methods). The crude was cooled down to room temperature and neutralized with 5% HCl to a pH of 7.00. To remove potassium salts and glycol by-products, the reaction crude was dissolved in water and dialyzed against water/ethanol and water. When the reaction was carried out in presence of DTAB or CTAB the resulting solution was passed through a strong cationic exchange column (High S Support) to remove the remaining cationic surfactant. The resulting solution was finally freeze-dried. A pure white powder corresponding to β-hydroxyalkyl ether of inulin was obtained with an average yield of about 80%.

2.4. Product characterization

The characterization of the 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-d6, 50 °C) of the alkyl chains and fructose units with less than a 10% of error (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-alkylepoxides, 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 Eq. (1).

$$RE\ (\%) = 100 \times \frac{\text{estimated DS}}{\text{theoretical DS}} \tag{1}$$

The stability study of inulin in KOH was done by incubating the 40% inulin solution in presence of sodium borohydride during 24 h in these high alkaline and temperature conditions by thin layer chromatography with acetone–water (9:1) as mobil phase. The absence of any product of degradation (fructose, glucose, sucrose, DP2, and other derivatives) indicates that inulin was stable at those conditions. A second method, Dionex-analysis (=anion exchange chromatography; gives qualitative indication of presence of all respective peaks corresponding to respective DP-fractions of inulin) combined with HPLC, was used to confirm the same results. Alkaline degradation of inulin and its structural implications were investigated last century (BeMiller, Steinheimer, & Allen, 1967).

3. Results and discussion

As indicated in the introduction, the synthesis of hydrophobic β-hydroxyalkyl ethers of inulin in aqueous media was recently reported in the literature under different conditions, including water–IPA mixtures. Our results indicated 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 was required to activate the hydroxyls of inulin. Furthermore, the etherification of inulin in water was limited by the hydrophobic effect due to the alkyl chain of the epoxide.

Table 1
Etherification of inulin with 1,2-dodecylepoxide using different structure and amount of surfactants[a].

Reaction	Surfactant	Surfactant concentration[b]	Solvent	RE (%)[c]
1[d]	–	–	Water	5
2[d]	–	–	Water/IPA	20
3	EC12	0.1	Water	6
4	CTAB	0.1	Water	10
5	CTAB	0.05	Water	36
6	DTAB	0.05	Water	31
7	DTAB	0.1	Water	51
8	DTAB	0.2	Water	49
9	DTAB	0.1	Water/IPA	6

[a] Reaction conditions: 40% inulin (w/w), KOH/AFU molar ratio: 0.37, epoxide/AFU molar ratio 0.2, 80–85 °C, 24 h.
[b] Equivalents of surfactant based on AFU. In all cases these concentrations are above their CMC.
[c] RE: reaction efficiency, an average of three experiments. Variability for reaction 7, 51 ± 3.6.
[d] Morros et al. (2010).

The more soluble the alkylepoxide, the higher its efficacy. It was described for the first time that short and medium chain length β-hydroxyalkyl ethers of inulin could be obtained in KOH 1 M water media at 80 °C using 40% inulin at reasonably good efficiencies and reaction times (Morros et al., 2010). Alkylepoxides with limited solubility in water reacted poorly in water/IPA media and efficiencies of about 20% were obtained.

In the present work, with the aim to increase the RE, the hydrophobic modification of inulin was carried out at the same basic aqueous solution already reported for short and medium β-hydroxyalkyl ethers of inulin performing the reaction in presence of a surfactant instead of water–IPA media (Morros et al., 2010). New water systems containing surfactants to obtain β-hydroxyalkyl ethers of inulin equal or longer than 12 carbon atoms in the hydrophobic chain were attempted. The influence of the amount and the structure of surfactant as well as the amount and the epoxide chain length on the RE was examined.

### 3.1. Influence of structure and amount of surfactant

Details of the synthesis and reaction efficiencies for inulin etherification with 1,2-dodecylepoxide in water with EC12, CTAB and DTAB at different concentrations are shown in Table 1. The reactions in water and in water/IPA mixtures already reported are depicted for comparative reasons.

First of all, a non-ionic surfactant at a concentration above its CMC was selected to study the effect of the epoxide emulsification on the synthesis of β-hydroxydodecyl ether of inulin. For this experiment EC12 was used as surfactant due to the good emulsification properties of this inulin derivative. Notice that the structure of EC12 is identical to that of the final β-hydroxydodecyl ether of inulin formed during the reaction. Even though the addition of a non-ionic surfactant such as EC12 at 0.1 equiv. (Table 1, entry 3) into the aqueous phase facilitated the epoxide emulsification, it did not increase the RE, giving the same values than those of the reaction in water (Table 1, entry 1). An increase in surfactant concentration in the media did not give significantly higher REs.

Cationic surfactants such as CTAB and DTAB instead of EC12 were then used as described in the literature for other polysaccharides (Durand, 2006). Initially, CTAB was used at 0.1 equiv. in water. At this concentration CTAB generated a high viscosity gel-like solution in which efficiency not higher than 10% was obtained because of the low diffusivity of the reactants in the media (Table 1, entry 4). Lower amounts of CTAB (0.05 equiv) resulted in a clear solution which was easily stirred giving a major increase of inulin modification by 1,2-epoxydodecane (36% efficiency, Table 1; entry 5).

In order to investigate the effect of the amount of cationic surfactant on the RE, we employed DTAB instead of CTAB at 0.05, 0.1 and 0.2 equiv. (Table 1, entries 6, 7 and 8). All reaction media were single-phase systems and the reactions were conducted under gentle stirring. Using DTAB at 0.05 equiv., a similar efficiency value to that of CTAB at 0.05 equiv. was also observed (31% efficiency, Table 1; entry 6). These increases in the efficiency values compared to that of EC12 could be attributed to the surfactant charge in the micelle and solubilisation. Increasing the DTAB concentration to 0.1 or 0.2 equiv., the RE was improved until values around 50% in both cases (Table 1, entries 7, 8). The efficiency of the reaction that contained water/DTAB/IPA is indicated in the entry 9 of Table 1. As expected, the water/DTAB/IPA systems produced a dramatic reduction of RE to values of 6% like in water alone. It is known that hydrophilic alcohols are solubilised in the aqueous solution and may affect the micellization process by modifying the solubility capacity of the solvent against the surfactant (Zana, 1995). The result of entry 9 shows the importance of the presence of cationic micelles in the catalytic system under study.
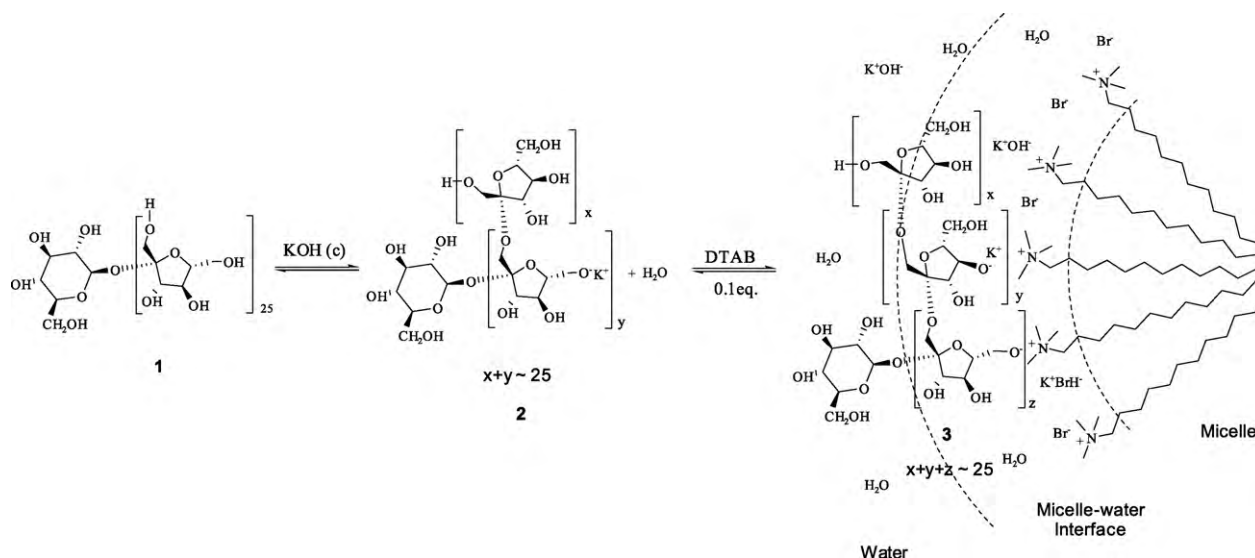
Scheme 1. Schematic representation of the inulin-KOH/DTAB micellar electrostatic interaction in water before the addition of epoxide.
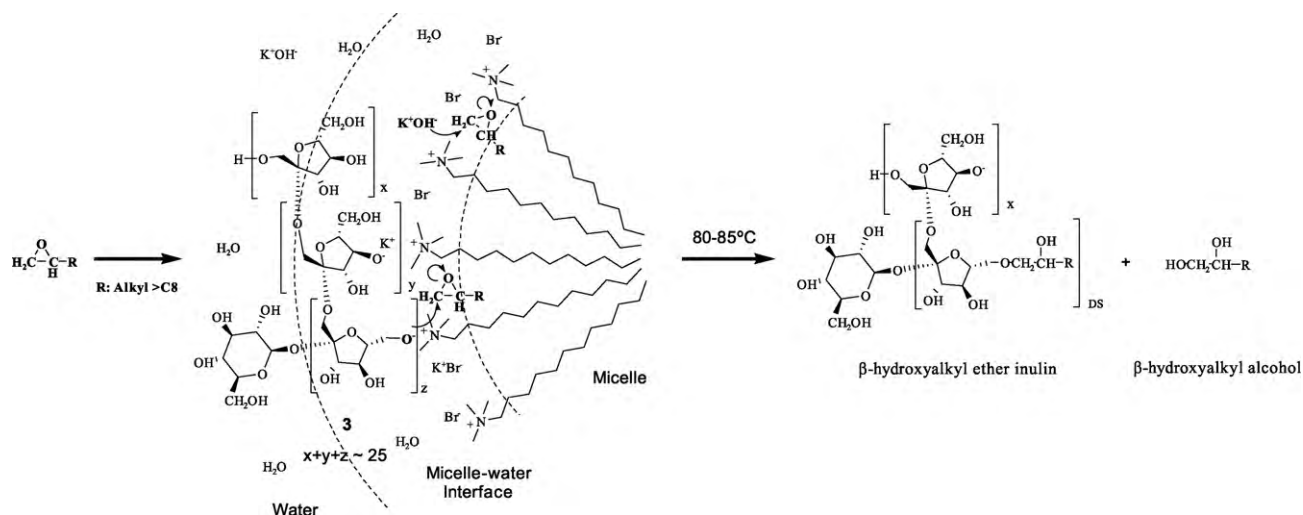
Scheme 2. Schematic representation of the inulin etherification after addition of 1,2-alkylepoxide in the DTAB micelle–water interface.

Considering the results of Table 1, we can state that the etherification of inulin in aqueous media with long chain 1,2-dodecylepoxide depends on the surfactant used. Non-ionic surfactants such as EC12 did not have any effect on the etherification reaction. On the contrary, the addition of cationic surfactants such as CTAB or DTAB showed a significant increase in REs.

In accordance with the results obtained by Durand (2006), the cationic charge of the surfactant had a strong influence on the etherification of polysaccharides with long alkylepoxides. The effect of DTAB micelles on this reaction could be attributed to both electrostatic (inulin/DTAB) and hydrophobic (epoxide/DTAB) interactions. A possible mechanism of the inulin etherification reaction in the system under study is shown in Schemes 1 and 2.

Scheme 1 shows the aqueous dynamic equilibrium of inulin between a positively charged DTAB-micelle surface and the bulk phase. The solubilised inulin (1) in presence of concentrated KOH aqueous solution is converted into a more reactive form with its hydroxyls ionized (2) through a normal acid-base equilibrium. Ionized 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 ionization produced by KOH, but also for the degree of association with the corresponding K^+. The displacement of K^+ and the solvation of water molecules to outer regions provoked by the electrostatic interaction between the cationic head group of DTAB and inulin provides an environment favourable to the desired O-ring opening epoxide reaction.

Scheme 2 displays how the insoluble 1,2-alkylepoxide (4) tends to be incorporated into the DTAB micelle. Since 1,2-alkylepoxide has both a polar and hydrophobic moieties, the polar region (oxirane ring) orientates itself toward the micelle–water interface formed by the head groups of the surfactant molecules, while the hydrophobic tail of the epoxide becomes involved with the hydrocarbon tails of the micelle core. The coexistence of both epoxide and ionized inulin in the micelle–water interface favours the O-ring opening reaction between them and hence the efficiency increased. The reaction yielded the β-hydroxyalkyl ether of inulin (5) and the glycol by-products due to epoxide hydrolysis (6).

In addition, optical micrographs of the reaction media as a function of temperature were realized. Fig. 1 shows the textures of the Inulin/KOH/DTAB/epoxide/water system at 25, 40, 60 and 80 °C. A gradual disappearance of the liquid crystal phase (Maltese cross) at 25 °C (Fig. 1a) to give a non-birefringent clear solution (micelles) at 80 °C (Fig. 1d) was observed. On the basis of this observation we can conclude that micellar systems are required to prepare the inulin ethers at reasonable reaction times (24 h).

3.2. Influence of the amount of epoxide

To study the influence of the amount of 1,2-dodecylepoxide on the RE, several syntheses were carried out in the system containing DTAB 0.1 equiv. varying the 1,2-alkylepoxide/AFU molar ratio.

Fig. 2 shows the RE of inulin etherification as a function of 1,2-dodecylepoxide/AFU molar ratio in the range 0.05 and 0.40. The values shown in Fig. 2 indicate that the system gave good RE values (50–65%) for 1,2-alkylepoxide/AFU molar ratios between 0.05 and 0.20. For concentrations above 0.20 the RE decreased until values of 15%. The low RE value at 1,2-dodecylepoxide/AFU molar ratio of 0.40 could be due to the limited solubilisation capacity of the DTAB micelles at DTAB 0.1 equiv. resulting in a biphasic system which favoured the formation of glycol by-products and/or polymerization.

3.3. Influence of epoxide chain length

Other epoxides with different chain lengths (OPh, C6, C10, C16 and C18/26) were tested in the system containing DTAB 0.1 equiv. Table 2 shows the reaction time and REs obtained for the tested 1,2-alkylepoxides.

Except for OPh (phenyl glycidyl ether), efficiencies of around 50% were obtained for all epoxides. Although longer times were required for longer epoxides, the catalytic system was appropriate for long chain epoxides. The efficiencies did not increase more than 50% and were not related to the epoxide alkyl chain. This fact could be due to the modification of the catalytic system dur-

Table 2
Etherification of inulin with different 1,2-alkylepoxides in DTAB micellar system[a].

Reaction	Chain	Time (h)	RE (%)
10	OPh	1	23
11	C6	4	50
12	C10	15	51
13	C12	18	54
14	C16	20	55
15	C18/26	24	45

[a] Reaction conditions: 40% inulin (w/w), KOH/AFU molar ratio: 0.37, epoxide/AFU molar ratio: 0.2.

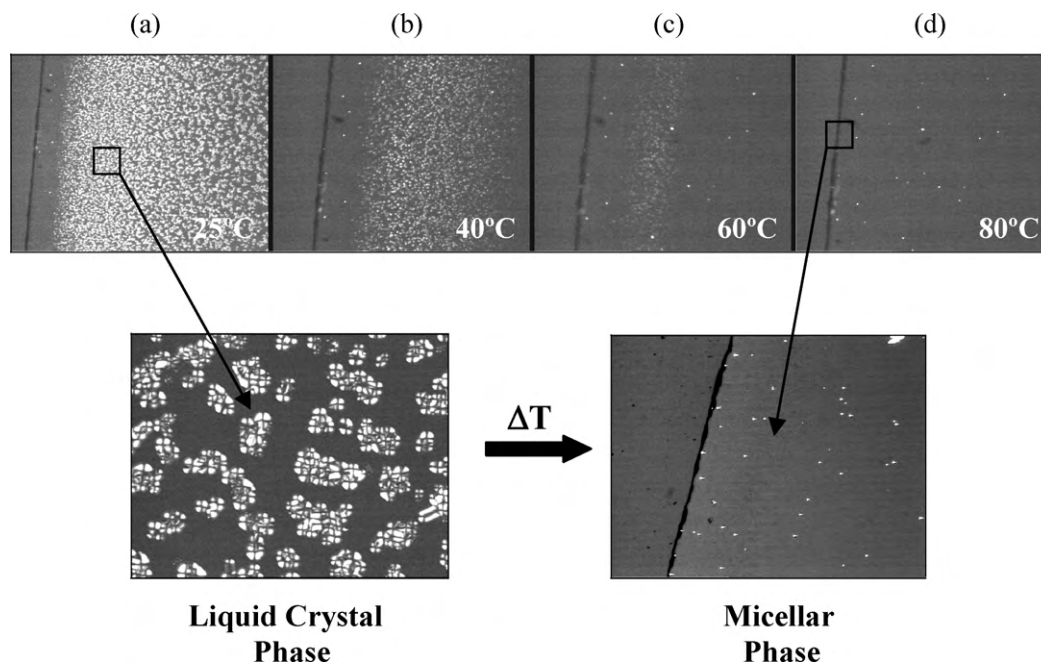**Fig. 1.** Optical micrograph (magnification 10×: (a) 25 °C, (b) 40 °C, (c) 60 °C, (d) 80 °C) and 40×: (a′) 25 °C, (d′) 80 °C) of the reaction media under the following reaction conditions: 40% inulin (w/w), KOH/AFU molar ratio: 0.37, epoxide/AFU molar ratio 0.2, DTAB/AFU molar ratio 0.1 at different temperatures.
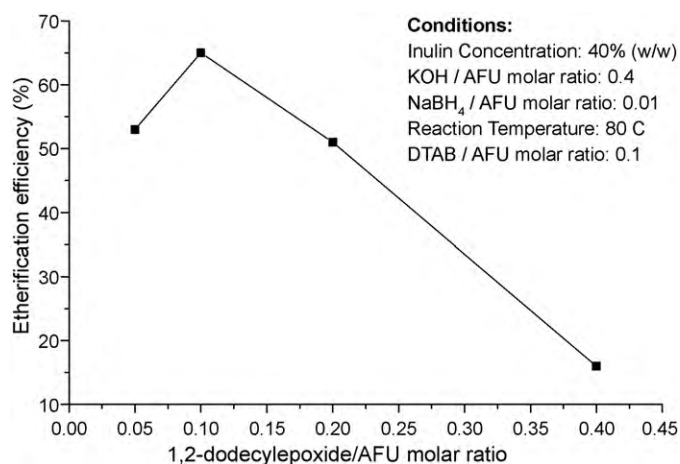

Fig. 2. RE of the etherification of inulin with different amounts of 1,2-dodecylepoxide in 0.1 DTAB/AFU molar ratio aqueous solution.

ing the reaction. The formation of a new non-ionic surfactant (β-hydroxyalkyl ethers of inulin) could affect the catalytic activity of the initial water/inulin/DTAB micellar system, modifying the aqueous dynamic equilibrium of inulin.

The low RE with OPh could be attributed to the presence of the polar phenyl group in the chain. The epoxide hydrolysis became more effective than inulin etherification because of the location of the polarizable phenyl group in outer regions. It is known that polar molecules are solubilised in the outer regions of micellar structures, whereas nonpolar solutes are contained in the inner micellar portions (Rosen, 2004).

4. Conclusions

β-Hydroxyalkyl ethers of inulin with long alkyl chains were obtained in aqueous basic micellar solutions. The etherification of inulin in aqueous media with 1,2-dodecylepoxide or longer depended on the surfactant used. DTAB was more efficient than

CTAB at 0.1 equiv. based on AFU. The effect of DTAB micelles on this reaction could be attributed to both electrostatic (inulin/DTAB) and hydrophobic (epoxide/DTAB) interactions. Efficiencies did not increase more than 50% and did not depend on variations in the epoxide alkyl chain length.

Acknowledgements

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Conditions:
Inulin Concentration: 40% (w/w)
KOH / AFU molar ratio: 0.4
NaBH₄ / AFU molar ratio: 0.01
Reaction Temperature: 80 C
DTAB / AFU molar ratio: 0.1

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