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Preparation of Long-Chain Alkyl Glucoside Surfactants by One-Step Direct Fischer Glucosidation, and by Transacetalation of Butyl Glucosides, on Beta Zeolite Catalysts

A. Corma[1], S. Iborra, S. Miquel, and J. Primo

Instituto de Tecnología Química, UPV-CSIC, Universidad Politécnica de Valencia, Avenida de los Naranjos s/n, 46022 Valencia, Spain
E-mail: acorma@itq.upv.es

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Long-chain alkyl glucoside surfactants have been obtained with good conversions and selectivities by the transacetalation of butyl glucosides with different fatty alcohols as well as by one-step direct glycosidation, using H-Beta zeolites as catalyst. The influence of the different process variables such as temperature, molar ratio of reactants, and fatty alcohol chain length has been investigated. Moreover, the study of the transacetalation process in the presence of H-Beta zeolites with different hydrophobic–hydrophilic properties has shown the strong influence of this zeolite property on catalyst deactivation. The rate of decay is lower for the more hydrophobic Beta samples. © 1998 Academic Press

INTRODUCTION

Alkyl glucosides are known to have several uses including their incorporation into detergent products as nonionic surfactants (1). In this case, they form micellar and vesicular microaggregates whose properties depend on the composition and structure of the carbohydrate head groups and on the length and shape of the hydrocarbon tail, as a result of a very fine balance of hydrophobic and hydrophilic interactions. As a consequence of this, alkyl glucosides with short and long hydrocarbon chains have different applications. For instance, octyl glucosides are being used extensively in biological membrane research (2) since they were found to be among the most effective detergents in releasing proteins from membrane-bounded compartments without denaturing them (3, 4). The alkyl glucosides derived from monohydric alcohol containing 8 to 20 carbon atoms can be prepared by the direct Fischer reaction (1, 5), but owing to the low solubility of glucose in a long-chain fatty alcohol the common approach involves a two-stage process (6, 7). In a first step, glucosides containing a shorter alkyl chain are prepared, and these, which are soluble in fatty alcohols, are transformed into a long-chain alkyl glucoside by means of a transacetalation reaction.

[1] To whom correspondence should be addressed.

In a recent work (8) it was shown that it is possible to prepare butyl glucosides in very good yields by means of the Fischer reaction in the presence of large-pore acid zeolite catalysts. The best results were obtained on a large-pore H-Beta zeolite, which, in addition to having an adequate topology, can easily be prepared with a large range of Si/Al ratios and consequently with different hydrophilic–hydrophobic characteristics (9).

In this paper we present the influence of the different process variables on the preparation of alkyl glucosides by transacetalation reaction of butyl glucosides with different fatty alcohols using zeolite Beta. The two-step procedure is compared with a single-step process, which involves the direct reaction of a higher alcohol with glucose.

EXPERIMENTAL

Materials

Anhydrous α-D-glucose and *n*-butanol obtained from Aldrich and Quimon, respectively, with a nominal purity >99%, were used without further purification. 1-octanol and 1-dodecanol were supplied by Aldrich with a nominal purity >99 and 98%, respectively.

The H-Beta-1 sample was supplied by PQ Corporation, in the acidic form and with a Si/Al of 13 (H-Beta-1). The H-Beta-2 was synthesized according to the method presented in Ref. (10) with a Si/Al ratio of 29 and with a marked hydrophobic character.

Reaction Procedure

Preparation of butyl glucosides. The zeolite catalyst was activated *in situ*, in a 10-ml batch glass reactor, by heating 0.075 g of the Beta zeolite at 353 K under vacuum (1 Torr) for 3 h. After this time, the system was cooled at room temperature and then *n*-butanol (NB) (5 ml, 0.054 mol) was introduced, followed by glucose (DG) addition (0.25 g, 0.0014 mol). The reaction mixture was heated at 393 K

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in a silicone oil bath and the catalyst was uniformly suspended as slurry in the butanol reaction solvent by stirring at 600 rpm. After 4 h reaction time the mixture was cooled at room temperature, dissolved with methanol, and filtered. Then, the filtered zeolite was submitted to solid–liquid extraction in a microsoxhlet using methanol and water as first and second solvents, respectively. The organic solutions, freed from the solvents and the remaining alcohol by evaporation in vacuum, were combined, weighed, analyzed by HPLC, and used as starting material for carrying out the second step, i.e., the transacetalation reaction.

Transacetalation process. For the transacetalation step, 40 wt.% zeolite according to the amount of butyl glucosides was activated, and 1-octanol (NO) or 1-dodecanol (ND) was added in the required proportion followed by the addition of the butyl glucoside. The reaction mixture was stirred and heated at 393 K under a vacuum of 400 Torr so that the *n*-butanol formed during the transacetalation was continuously removed. In order to follow the evolution of the reaction, samples were taken at regular time intervals. The filtered zeolite remaining in the microsyringe was extracted with methanol and water as first and second solvents, respectively. The different products were analyzed by HPLC, adding a known amount of methyl-α-D-glucopyranoside as internal standard. At the end of the reaction, the reaction mixture and the catalyst were treated as described above for the preparation of butyl glucoside. Mass balances were performed in each experiment and the recovered products accounted for >95% of the reactants.

The one-step direct acetalization of glucose with 1-octanol and 1-dodecanol. For the direct Fischer glucosidation, 0.25 g zeolite catalyst was activated *in situ*, in a 10-ml batch glass reactor, by heating at 353 K under vacuum (1 Torr) for 3 h. After this, the system was cooled to room temperature and then the alcohol (3 ml, 0.019 mol of 1-octanol or 0.013 mol of 1-dodecanol) was introduced. The system was heated at 393 K, and 0.05 g (0.27 mmol) glucose were added. For kinetic purpose, this was considered the zero reaction time. At 30-min intervals, constant amounts of glucose were manually added to the system. With 1-octanol, glucose was added in increments of 0.1 g (0.55 mmol), until 0.85 g (4.72 mmol), while with 1-dodecanol, glucose was added in increments of 0.07 g (0.38 mmol), until 0.6 g (3.33 mmol) in order to reach in both cases a final alcohol/glucose ratio of 4. With the aim of following the evolution of the reaction, before each glucose addition, a sample was taken, filtered, and analyzed by HPLC, adding methyl-α-D-glucopyranoside as the internal standard. One-half hour after the last incremental addition, the reaction was stopped by cooling at room temperature. Then, the product mixture and the catalyst were treated as previously described for the preparation of butyl glucosides. Mass balances were performed in each experiment and the recovered products accounted for >95% of the reactants.

HPLC analyses were performed with a system formed by a Waters pump (model 510) and a Waters 410 differential refractometer using a HYPERSIL-APS-25 μm (250 × 0.46 mm) column. In order to deal with the less polar products, the column was eluted with an acetonitrile/water mobile phase composed of 5% water, while 20% water was used for the more polar products. In both cases, the flow of the mobile phase was 1 ml/min. Preparative scale HPLC was performed using a HYPERSIL-APS-25 μm (250 × 1 mm), and in this case the flow of the mobile phases was 4 ml/min.

^{1}H and ^{13}C NMR of the products isolated from the reaction mixture were done in a Varian 400WB instrument and were identified by comparison with the NMR spectra of butyl, octyl, and dodecyl glucosides reported in the literature (11–13).

RESULTS AND DISCUSSION

The Transacetalation Process

As described above, the first reaction step was carried out at 393 K in the presence of a H-Beta-1 zeolite with a Si/Al ratio of 13 and a *n*-butanol/glucose ratio (NB/DG) of 40. After 4 h reaction time, the yields of butyl furanoside and butyl pyranoside were 10 and 90%, respectively, and this mixture was the starting feed for carrying out the transacetalation reaction.

The reaction between the mixture of butyl glucosides (BG) and NO in a BG/NO ratio of 12 was carried out at 393 K and 400 Torr, in the presence of H-Beta-1 zeolite. The results obtained (Fig. 1) show that anomeric mixtures of two octyl glucoside isomers, the (α,β)-octyl furanoside (**3a**) and the (α,β)-octyl pyranoside (**4a**), were formed. Both glucosides appear as primary products, and consequently the global reaction can be written as presented in Scheme 1.

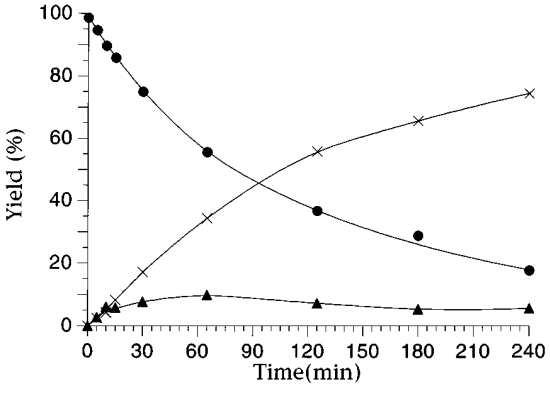
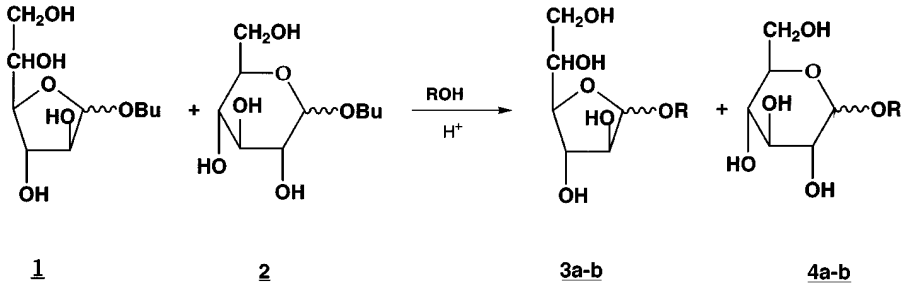


FIG. 1. Time conversion plot of butyl glucosides (**1** + **2**, ●) to octyl glucofuranoside (**3a**, ▲) and octyl glucopyranoside (**4a**, ×) at 393 K in the presence of H-Beta-1 and starting from an initial **1**/**2** ratio of 10/90.



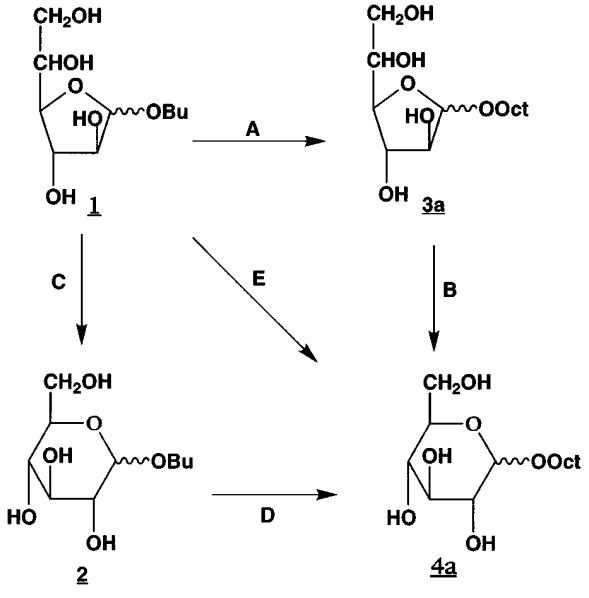
	R
a	$-(CH_2)_7CH_3$
b	$-(CH_2)_{11}CH_3$

SCHEME 1

In a first approximation it is reasonable to expect that the reaction leading to the formation of the octyl glucofuranoside (**3a**) will be the transacetalation of the butyl glucofuranoside (**1**) (step A, in Scheme 2). On the other hand, the formation of the octyl glucopyranoside (**4a**) can occur by the transacetalation of the butyl glucopyranoside (**2**) (step D), the isomerization of the octyl glucofuranoside (**3a**) (step B), or even the isomerization of the butyl glucofuranoside (**1**) followed by the transacetalation of the intermediate molecule during the ring opening (step E) (14a).

In order to study in greater detail the mechanism of the transacetalation, this reaction was again carried out at 393 K and 400 Torr but starting now with a reaction mixture formed by 30 and 70% of butyl pyranoside and butyl furanoside, respectively, instead of the 90 and 10%, respectively, used before. The rest of the reaction variables were kept the same. The kinetic results presented in Fig. 2a clearly show that, in this case, the amount of butyl glucopyranoside (**2**) first increases with time, goes though a maximum, and then decreases. On the other hand, the butyl glucofuranoside (**1**) continuously decreases to almost complete consumption. In the case of the octyl glucofuranoside (**3a**), this is rapidly formed and then the concentration diminishes while the octyl glucopyranoside (**4a**) continuously increases with time (Table 1).

Taking into account the evolution of reactants and products with reaction time (Table 1 and Fig. 2a), we can say that the butyl furanoside not only undergoes an isomerization to the corresponding pyranoside but also a transacetalation to the primary and unstable octyl furanoside. Consequently, the octyl pyranoside is formed by two different routes: the isomerization of the octyl furanoside to the thermodynamically more stable six member ring compound and the direct



SCHEME 2

TABLE 1

Initial Disappearance Rates of Butylglucosides and Distribution of Products Obtained at Two Conversion Levels, Starting from Two Different Initial Mixture Compositions in Butyl Glucosides

Compounds	Initial mixture composition	Initial disappearance rates of butylglucosides (mol h^{-1} g^{-1}) $\times 10^3$	Mixture composition at different conversions	
			55%	70%
1	70	15	2	2
2	30		43	28
3a	0		19	12
4a	0		36	58
1	10	5.2	0	0
2	90		45	28
3a	0		9	5
4a	0		46	67

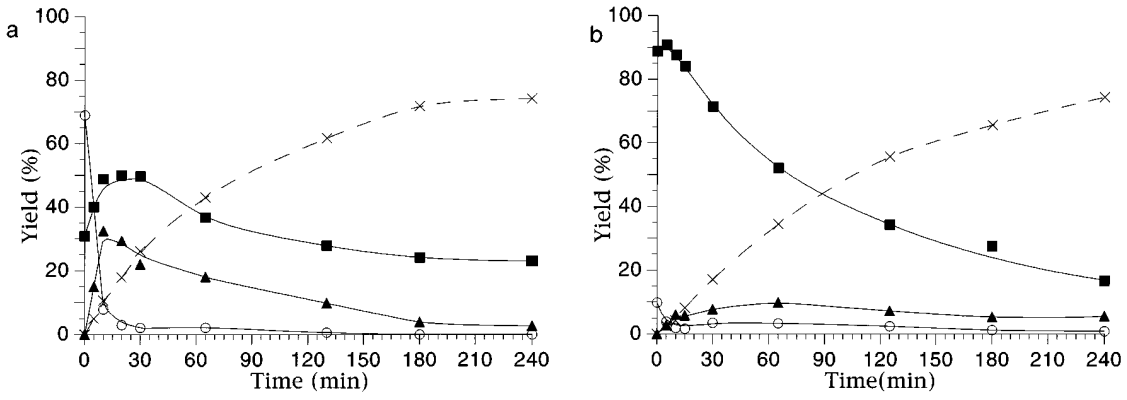


FIG. 2. Time conversion plot of butyl glucofuranoside (**1**, o) and butyl glucopyranoside (**2**, ■) to octyl glucofuranoside (**3a**, ▲) and octyl glucopyranoside (**4a**, ×) at 393 K in the presence of H-Beta-1 and starting from an initial **1**/**2** ratio of 70/30 (a) and 10/90 (b).

transacetalation of the butyl pyranoside initially present in the starting mixture. However, we do not reject that the transacetalation of a possible open intermediate form, giving rise to the direct formation of the octyl glucopyranoside, can also occur. Nevertheless, as the formation of **3a** is kinetically favored (14, 15), we can suppose that, if this reaction takes place, its contribution to the final product will be small (Scheme 2).

As we can observe in Table 1, the initial rate of disappearance of the butyl glucosides is strongly influenced by the feed composition. However, the final compositions achieved with the two different feeds are similar, and only the selectivities to octyl pyranoside and octyl furanoside seem to be slightly affected by the initial composition of the mixture; i.e., starting from a higher concentration of butyl furanoside we obtain a richer final composition in octyl furanoside.

In any case, taking into consideration that the octyl furanoside and the octyl pyranoside present similar detergency properties, the total conversion of the butyl glucosides becomes more important than the distribution of the two isomers when one is interested in the application of the glucosides as environmentally friendly detergents. Thus, from the results presented in Table 1 and Figs. 2a and 2b, it becomes clear that starting with a mixture rich in butyl furanoside (70%) the reaction rate is higher, and a larger total conversion is reached in shorter reaction times.

Influence of the reaction temperature. To study the influence of the reaction temperature on the transacetalation process, we have carried out the reaction in the presence of H-Beta-1, at 383 and 393 K, starting from a mixture of butyl glucopyranoside and butyl glucofuranoside of 90 and 10%, respectively, using 1-octanol as the second alcohol in a NO/BG ratio of 12 and under 400 Torr. The kinetic results obtained are given in Figs. 1 and 3. It is possible to see that a 10° increase in the reaction temperature produces a 2.5 increase in the initial rate of the disappearance of the butyl glucosides, which implies an apparent activation energy of ~27 Kcal mol^{-1} for the transacetalation process. This value is close to the activation energy obtained for the glucosidation of glucose with butanol (8) and also similar to the activation energy of the transacetalation process when the reaction is carried out using liquid acids in a single-phase process. These results indicate not only that one could strongly influence the rate of the transacetalation reaction by increasing the temperature but also that in the solid–liquid process studied here, the reaction is not controlled by the diffusion of reactants or products in the solid. Nevertheless, it should be taken into account that with temperatures significantly greater than 393 K, side reactions may increase faster than the primary reaction, giving rise to a poor quality product (16).

Influence of the chain length of the alcohol. The alkyl chain linked to the sugar residue of the alkyl glucoside is compatible with nonpolar environments, whereas their hydroxyl groups are responsible for the high solubility in

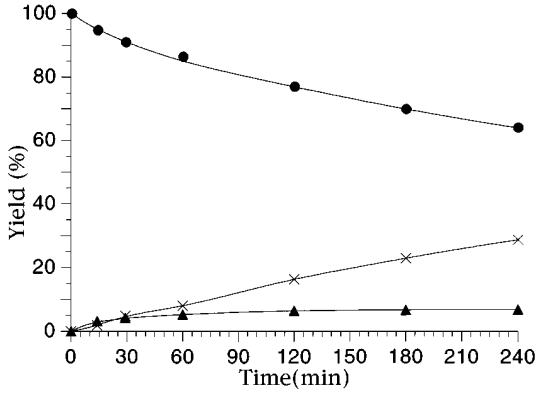


FIG. 3. Time conversion plot of butyl glucosides (**1** + **2**, ●) to octyl glucofuranoside (**3a**, ▲) and octyl glucopyranoside (**4a**, ×) at 383 K in the presence of H-Beta-1 and starting from an initial **1**/**2** ratio of 10/90.

water. The length of the alkyl chain has a direct influence on the alkyl glucoside solubilizing abilities and has the most pronounced effect on the critical micelle concentration (CMC) (17). It is known that short-chain alkyl glucosides do not provide any detergency benefits (1, 18), and only for alkyl chains above C8 is a drastic decrease of the CMC with increasing alkyl chain observed (6). It is then of interest to have a process flexible enough to produce alkyl glucosides with different alkyl chains. This has been studied here by also performing the transacetalation of butyl glucosides with 1-dodecanol.

Starting from the same initial mixture (**2**/**1** = 9), the reaction was carried out using 1-dodecanol as secondary alcohol at 393 K and in a molar ratio BG/ND = 12. The results obtained show the formation of the two expected isomers, the dodecyl glucofuranoside (**3b**) and the dodecyl glucopyranoside (**4b**) (Fig. 4), while the initial rate and the final conversion are smaller for the transacetalation of the longer alcohol, which would need a longer reaction time to reach interesting levels of conversion.

Catalyst deactivation. From the engineering point of view, it will be of interest to carry out the two reaction steps, i.e., glucosidation with *n*-butanol and transacetalation of the butyl glucosides with 1-octanol, in a single pot, avoiding separation of the catalyst and its removal after the first step has occurred. However, in order to be able to do this economically, little or no deactivation of the catalyst has to occur during the glucosidation with *n*-butanol. To study this, we have carried out a new series of experiments using in both steps an alcohol/glucoside ratio of 12 (mol mol^{-1}) starting from a mixture of butyl glucopyranoside and butyl furanoside of 90 and 10%, respectively, and using 1-octanol as the second alcohol. In one case, after distillation of the butanol we have added it directly to the reactor without changing the catalyst, while in the second case, the used catalyst was separated and new fresh catalyst was added just before adding the 1-octanol and performing the transacetalation. After 4 h reaction time, the results presented in Table 2 were obtained. It can be seen there that when the same sample of catalyst was used to carry out the two steps, the initial rate of the transacetalation reaction was 25% lower than when fresh catalyst was introduced to perform it. The results indicate that some deactivation of the catalyst does indeed occur during the glucosidation process. After 4 h reaction time, the fresh catalyst (H-Beta-1) still gives a much higher conversion than the used catalyst (Table 2). In a previous paper, we demonstrated the importance of the hydrophobic–hydrophilic properties of the catalyst on activity (9). It can then be expected that those catalyst properties will also have a strong impact on catalyst deactivation. In order to study this we have repeated the above experiments with a hydrophobic Beta zeolite (H-Beta-2 with Si/Al = 29). The results presented in Fig. 5 show that with zeolite H-Beta-2, which is more hydrophobic than H-Beta-1, there is also an initial deactivation. However, after 4 h reaction time the same conversion was achieved with the fresh (Fig. 5a) and with the used catalyst (Fig. 5b). This can indicate that with this catalyst, there is some deactivation that occurs in the first period of time and then the activity levels off. In any case it appears that the deactivation of the catalyst during the first step, i.e., the formation of the butyl glucoside, does not impede carrying out of the second step in very reasonable reaction times.

We have analyzed the products remaining adsorbed after the reaction and the extractions with soxhlet, and they are composed mainly of alkyl glucosides and of little amounts of glucose. When these products are burned off by calcination at 500°C, the initial activity is completely restored. The fact that some deactivation occurs in the first step may imply in some cases the need to separate the catalyst after this and to add new catalyst for carrying out the second step of the global reaction, i.e., the transacetalation. Such an inconvenience strongly encouraged us to perform the glucosidation of glucose with long-chain alcohols in one step, thereby avoiding the transacetalation reaction required in the conventional process. We return later to this point.

TABLE 2

Results Obtained in the Two-Step Process for the Production of Octyl Glucosides without and with Addition of Fresh Catalysts during the Transacetalation Step and Starting from a Butyl Glucoside Mixture 2/1 of 9, in the Presence of the H-Beta-1 Zeolite at 393 K after 4 h Reaction Time

Catalyst	Initial rate of butylglucosides disappearance (mol h^{-1} g^{-1}) × 10^3	Yields (%)			
		1	**2**	**3a**	**4a**
Renovated	5.2	0	19	5	76
Same	4	0	33	7	60

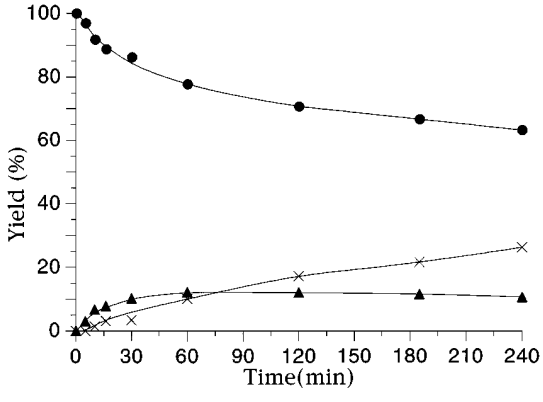


FIG. 4. Time conversion plot of butyl glucosides (**1** + **2**, ●) to dodecyl glucofuranoside (**3b**, ▲) and dodecyl glucopyranoside (**4b**, ×) at 393 K in the presence of H-Beta-1 and starting from an initial **1**/**2** ratio of 10/90.

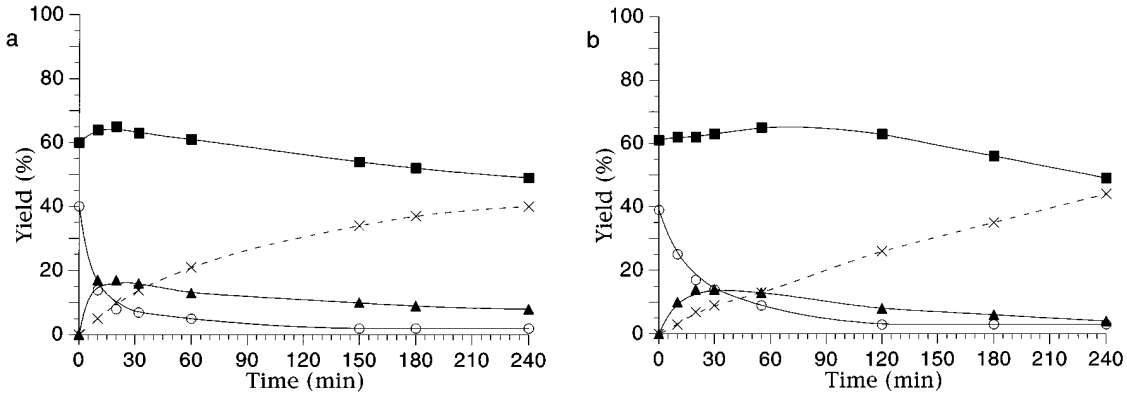


FIG. 5. Time conversion plot of butyl glucofuranoside (**1**, o) and butyl glucopyranoside (**2**, ■) to octyl glucofuranoside (**3a**, ▲) and octyl glucopyranoside (**4a**, x) at 393 K (a) in the presence of fresh H-Beta-2 and (b) without renovating the catalyst (H-Beta-2) and starting from an initial **1**/**2** ratio of 40/60.

Influence of the NO/BG ratio. From an economical point of view it is important to minimize the alcohol-to-glucose ratio while keeping the rate of the reaction and the selectivity to alkyl monoglucosides at reasonable levels. In order to study the former variable, the second step of the reaction was carried out using a NO/BG of 12, 7, 4, and 2 (mol mol^{-1}) and starting from a mixture composition of **2**/**1** of 9.

The results from Fig. 6 clearly show the same behavior we observed (8) for the first step of the reaction; i.e., the formation of octyl glucosides increases to a NO/BG of 7 and then remains practically unchanged. However, most of the gain in reaction rate has already been achieved at a NO/BG ratio of 4.

In conclusion, it is possible to obtain good conversions to glucosides containing hydrophobic chains by transacetalation reaction of butyl glucosides with fatty alcohols using H-Beta zeolite as catalyst. The transacetalation is best carried out starting with a feed composition rich in butyl furanoside. In the case of transacetalation with 1-octanol, ratios of NO/BG of 4 and above are required.

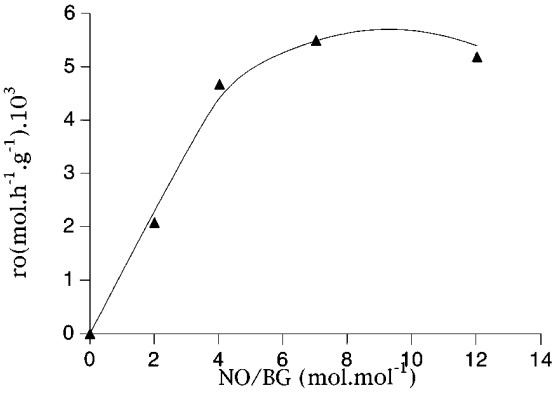


FIG. 6. Influence of the 1-octanol/butyl glucoside molar ratio on the initial rate (mol h^{-1} g^{-1} 10^3) of formation of octyl glucosides at 393 K in the presence of H-Beta-1.

The Direct Reaction of a Long-Chain Alcohol with Glucose

There is no doubt that it will be very interesting to manufacture higher alkylglucosides in a single step. The main problem one may encounter with this is the low solubility of glucose in long-chain alcohols with the corresponding negative effect on reaction rate and on the quality of the final product. For instance, the solubility of D-glucose in 1-octanol at 90°C is quite low (~1.6 g l^{-1}) (1). Nevertheless it should be possible to overcome this limitation using an excess of alcohol and adding incremental amounts of glucose (19). Then, when a certain amount of the higher alkylglucosides are formed, the reaction will be favored since the alkyl glucoside acts as an emulsifier stabilizing the monophasic system.

In order to verify this hypothesis, two reactions were carried out, as indicated above, using 1-octanol (Fig. 7) and 1-dodecanol (Fig. 8) as the alcohol, and in the presence of

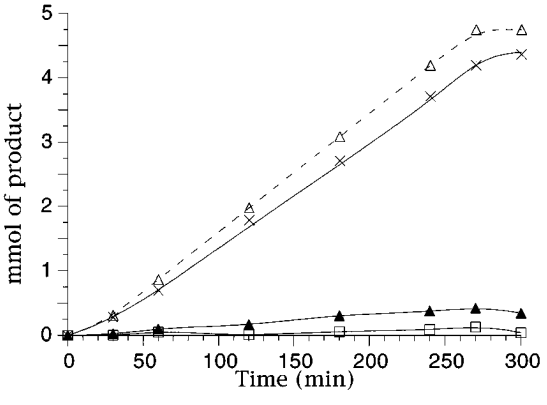


FIG. 7. Amount (mmol) versus time of the products obtained in the direct acetalization of D-glucose (□) with 1-octanol at 393 K: octyl glucofuranoside (**3a**, ▲) and octyl glucopyranoside (**4a**, ×). Amount of octyl glucosides that would be obtained if all the added D-glucose were converted (△).

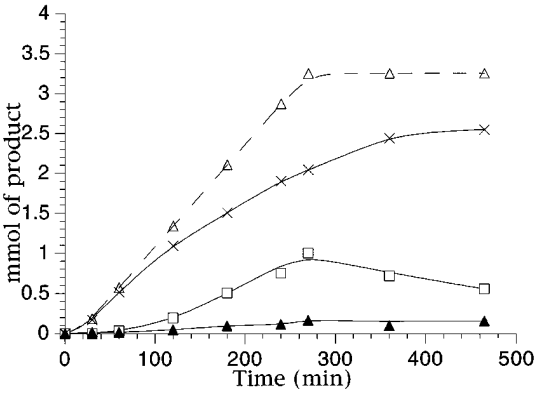


FIG. 8. Amount (mmol) versus time of the products obtained in the direct acetalization of D-glucose (□) with 1-dodecanol at 393 K: octyl glucofuranoside (**3b**, ▲) and dodecyl glucopyranoside (**4b**, ×). Amount of octyl glucosides that would be obtained if all the added D-glucose were converted (△).

H-Beta-1. The results presented in these figures indicate (dashed line) the amount of alkyl glucoside (expressed in mmol) that would be obtained if all the added glucose were converted in each step. The continuous lines represent the experimental values obtained. It can be seen that, in both cases, the glucose readily reacts, giving as the only products the two alkyl glucoside isomers expected. In the presence of 1-octanol and for each increment, the conversion is almost complete, indicating first that the addition of the glucose to the reaction mixture is carried out over an adequate periodic time interval and second that the quantity added is an acceptable amount. On the other hand, in the presence of 1-dodecanol the conversion reached after each stage is lower. After 4 h reaction, no further glucose was added and the conversion was still monitored. It was found that allowing more time led to an increase in the conversion, showing that the catalyst is still presenting activity. We can therefore easily suppose that a better conversion can be reached by adding in each step a lower amount of glucose or using a longer interval time between each addition. These results prove that it is possible, using H-Beta zeolite as the catalyst, to prepare, in one step and with good conversions and excellent selectivities, alkyl glucosides with an alkyl chain above C8, starting directly from glucose and the high alcohol. These results suggest that there is a possibility for the commercial application of zeolites in the preparation of long-chain alkylglucosides (20).

CONCLUSIONS

In the present work, we have elucidated the possibility of obtaining long-chain alkyl glucoside surfactants with high conversions and selectivities by the transacetalation of butyl glucosides with fatty alcohols in the presence of H-Beta zeolite as the catalyst. Furthermore, we have found that the initial rate of disappearance of butyl glucosides is strongly influenced by the feed composition, and a higher amount of butyl glucofuranosides gave rise to a higher reaction rate and a larger total conversion over shorter reaction time. The hydrophobic H-Beta zeolite proved to present a better resistance to deactivation during the transacetalation process. Moreover, for this two-step reaction, ratios of fatty alcohol to butyl glucosides of 4 and above were found to give a good initial reaction rate minimizing side reactions. Finally, it is possible to prepare alkyl glucosides with an alkyl chain above C8, starting directly from glucose and fatty alcohol, obtaining good conversions and excellent selectivities to the long alkyl glucoside surfactant.

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