Selective synthesis of amphiphilic hydroxyalkylethers of disaccharides over solid basic catalysts
Influence of the superficial hydrophilic–lipophilic balance of the catalyst

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Abstract

The direct etherification of three disaccharidic polyols, sucrose, trehalose and isomalt®, with 1,2-epoxydodecane was studied. The catalytic activity of various solid basic catalysts, differing by their superficial hydrophilic–lipophilic properties, was investigated. Disaccharide hydroxy-alkylethers yields greater than 90% were obtained in a DMSO–water mixture in the presence of the recoverable PS–NOH solid catalyst. The regioselectivity of the reaction was fully investigated by HPLC and NMR.
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1. Introduction

During the last decades, intense researches have been directed towards the chemical potentialities of agroresources [1]. Indeed, this huge natural carbon reserve offers many advantages for chemists such as renewability, biodegradability, biocompatibility and wide diversity. In this respect, carbohydrates are a very important class of natural organic building blocks notably for the synthesis of non-ionic surfactants [2]. Among biobased feedstock surfactants, many are obtained by direct esterification of natural polyols either with fatty acid or fatty methyl ester through catalytic or enzymatic processes [3]. However, the instability of the resulting ester link under basic conditions often limits their industrial applications. For this reason we have studied the etherification of various disaccharides with a fatty epoxide which should afford more chemically resistant surfactants than those commonly used. The one pot and selective etherification of unprotected carbohydrates remains a difficult challenge as only the derivatives with low substitution degrees are liable to present the most useful surfactants properties. In a preliminary paper, we described that basic anion exchange resins were very efficient solid catalysts for the one step production of sucrose monohydroxyalkylethers [4]. Notably, we showed that the activity of the solid catalyst was closely related to its basicity and to the solubility of the epoxydodecane in the catalytic phase. On the continuation of this work, we wish to discuss here: (i) the key role played by the lipophilic properties of the catalytic surfaces on the reaction selectivity; (ii) the extension of the catalytic process to two other disaccharides such as trehalose (α-D-glucopyranosyl-α-D-glucopyranose) and isomalt® (mixture of 1-O-(α-D-glucopyranosyl)-D-mannitol and 6-O-(α-D-glucopyranosyl)-D-sorbitol) with the aim of produc-

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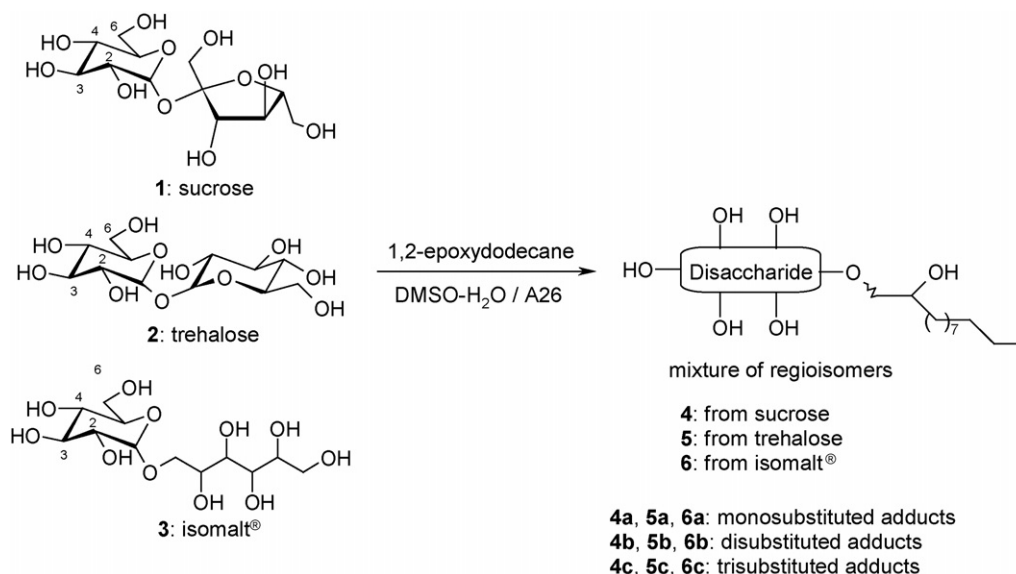
Scheme 1. Catalytic etherification of disaccharides over A26 anion exchange resin.

ing new non-ionic and potentially safer surfactants (Scheme 1) [5]; (iii) the regioselectivity of the catalytic process; (iv) the preliminary physicochemical data on the prepared amphiphilic molecules.

2. Experimental

2.1. Chemicals

Both anion exchange resins PS–NMe$_2$ and PS–NOH and all disaccharides used in this study were kindly provided by Rohm and Hass and TEREOS, respectively. Strongly basic quaternary ammonium type-I anion exchange resin PS–NOH (A26; OH$^-$ form) is a polystyrene network cross linked with 2% of divinylbenzene and functionalized with 4.40 mmol of hydroxide anion per gram of dry resin. The PS–NOH catalyst contains 67–73 wt.% of water and a particle size distribution in the range 0.4–1.2 mm. PS–NMe$_2$ (A21) is a weakly basic anion exchange resin functionalized with 4.7 mmol/g of dimethyl-amino groups grafted over a polystyrene network crosslinked with 2% of divinylbenzene. The PS–NMe$_2$ catalyst contains 54–60 wt.% of water and a particle size distribution in a range 0.4–1.2 mm. Prior to use, PS–NOH and PS–NMe$_2$ catalysts were washed several times with distilled water and dried by extensive washing with 95% ethanol and diethylether. 1,2-Epoxydodecane, dimethylsulfoxide were purchased to Sigma–Aldrich and used as received without further purifications.

2.2. Analytical methods

The reaction progress of sucrose etherification was monitored on a Shimadzu HPLC (SIL 10A) equipped with a column Touzard & Matignon Nucleosil C8 (250 mm × 4.6 mm) and using a methanol/water mixture (78:22) as eluent with a flow of 0.8 mL min^{-1}, and detection by differential refracto-

metry (Waters 2410). After external calibration, this analytical method allowed the quantification of 1,2-epoxydodecane, 1,2-dodecanediol, sucrose, trehalose, isomalt$^\circledR$ and the resulting mono-, dihydroxyalkylethers. The regioselectivity of the reaction was determined by semi preparative HPLC (column NH$_2$, CH$_3$CN/H$_2$O 90/10, 20 mL/min).

2.3. General procedure for the synthesis siliceous materials

Chlorobenzyl silica (chlorine content: 2.5 mmol/g), used as siliceous precursor, was prepared as described in the literature [6].

2.3.1. SiO$_2$–NMe$_2$

A 1 g of freshly prepared chlorobenzyl silica was suspended in 20 mL of toluene and heated at 50 °C. Dimethylamine gas was then bubbled into the solution for 24 h. The siliceous material was collected by filtration and washed with a strongly basic solution of 1,5,7-triazabicyclo[4.4.0]dec-5-ene (0.1 M) in acetonitrile in order to remove dimethylammonium chloride formed as side product during the grafting process. The solid was finally purified by soxhlet extraction with acetonitrile before to be dried overnight in an oven at 50 °C (10^{-1} mmHg).

Elemental analyses: %C: 23.23; %H: 3.24; %N: 2.13.

2.3.2. SiO$_2$–Im

A 1 g of freshly prepared chlorobenzyl silica and 1.63 g (20 mmol) of 2-methylimidazole were mixed in 10 mL of dimethylformamide and stirred at reflux for 20 h. The siliceous material was collected by filtration and, as described above, washed with a basic solution of 1,5,7-triazabicyclo[4.4.0]dec-5-ene (0.1 M) in acetonitrile. The solid was finally purified by soxhlet extraction with acetonitrile before to be dried overnight in an oven at 50 °C (10^{-1} mmHg).

Elemental analyses: %C: 19.12; %H: 3.31; %N: 3.69.

2.4. General procedure for the synthesis PS–Im

A 2 g of Merrifield's resin (chlorine content of 2.6 mmol/g) was suspended in 10 mmol of dimethylformamide in the presence of 2 g (24 mmol) of 2-methylimidazole and 0.64 g (5.8 mmol) of Na_2CO_3. The resulting solution was stirred at reflux for 20 h. The PS–Im was collected by filtration, washed with dichloromethane, then with water till neutral pH and with acetone.

Elemental analyses: %C: 76.75; %H: 6.92; %N: 6.19.

2.5. General procedure for the etherification of disaccharides over solid catalysts

In a round bottom flask, equipped with a condenser and a mecanical stirring, disaccharides **1–3** (10 mmol) were mixed with 1,2-epoxydodecane (2.5 mmol) in 5 mL of the desired DMSO/H_2O composition (Tables 1 and 3). The resulting mixture was then heated, under nitrogen atmosphere, at 110 °C in neat DMSO or at 100 °C in DMSO/H_2O mixtures before addition of the solid catalyst (0.1–0.7 equiv. of supported catalytic sites). The reaction progress was monitored by HPLC. After total consumption of the 1,2-epoxydodecane, the solid catalyst was recovered by filtration. When a DMSO–H_2O mixture was used as solvent, the recovered PS–NOH catalyst was washed with DMSO and H_2O and reused as collected without any further purification. Yields are given in Tables 1 and 3.

2.6. Characterization

Sucrose ethers **4** have already been fully described in a previous paper [7].

2.6.1. Characterization of 5a–c

Mono-, di- and triahydroxyalkylethers of trehalose **5a–c** were separated over silica chromatography using an eluent CH_2Cl_2/MeOH/acetone/water: 67/10/10/2,5. After freeze-drying, a white powder was obtained for **5a** and **5b** whereas a yellow oil was obtained for **5c**.

2.6.1.1. Mono-O-(2-hydroxydodecyl)trehalose (5a) (mixture of regioisomers). ^{1}H NMR (300 MHz, D_2O) δ (ppm): 0.85–0.95 (m, 3H, Me); 1.20–1.50 (m, 18H, $(CH_2)_9$); 3.20–4.05 (m, 15H, C*H*OH, C*H_2*OH, OC*H_2*); 5.15–5.40 (m, 2H, H-1, H-1′); SM-HR (FAB+): m/z calculated for $C_{24}H_{47}O_{12}$ [MH]+: 527.3067. Found: 527.3068; elemental analysis: calculated for $C_{24}H_{46}O_{12}$ (with 1,5 H_2O): C, 52.06; H, 8.92; O, 39.01; found: C, 51.84; H, 8.93; O, 38.71.

Each regioisomer of mono-*O*-(2-hydroxydodecyl) trehalose **5a** was purified by semi preparative HPLC (column NH_2, CH_3CN/H_2O 90/10, 20 mL/min). It is worth noting that these products cannot be considered as pure materials since, for each position of the fatty chain on the carbohydrate, a 1:1 mixture of epimers was obtained at the hydroxyalkyl linkage.

2.6.1.1.1. 2-O-(2-Hydroxydodecyl) trehalose. First epimer. ^{1}H NMR (500 MHz, MeOD): δ (ppm) 0.85–0.88 (t, 3H, J = 7.0 Hz, CH_3); 1.20–1.50 (m, 18H, $(CH_2)_9$); 3.24 (pseudo t, 1H, $J_{3,4} = J_{4,5} = 9$, 6 Hz, H-4); 3.26 (dd, 1 H, $J_{1',2'} = 3.5$ Hz, $J_{2',3'} = 9.6$ Hz, H-2′); 3.34 (dd, 1 H, $J_{3',4'} = 9.1$ Hz, $J_{4',5'} = 9.9$ Hz, H-4′); 3.46 (dd, 1H, $J_{1,2} = 3.8$ Hz, $J_{2,3} = 9.8$ Hz, H-2); 3.55 (d, 2H, $J_{OCH_2,CHOH} = 5.7$ Hz, OC*H_2*); 3.62 (dd, 1H, $J_{6a,6b} = 12.0$ Hz, $J_{5,6b} = 6.2$ Hz, H-6b); 3.66 (dd, 1H, $J_{6'a,6'b} = 12.0$ Hz, $J_{5',6'b} = 5.2$ Hz, H-6′b); 3.68–3.74 (m, 1H, C*H*OH); 3.70 (pseudo t; 1H, H-3); 3.76 (dd; 1H, $J_{5',6'a} = 2.2$ Hz, H-6′a); 3.80 (dd, 1H, $J_{5,6a} = 2.2$ Hz, H-6a); 3.84 (ddd, 1 H, H-5′); 3.86 (pseudo t, 1 H, H-3′); 3.90 (ddd, 1 H, H-5′); 5.08 (d, 1H, H-1); 5.28 (d, 1H, H-1′); ^{13}C NMR (125 MHz, MeOD): δ (ppm) 14.5 (CH_3), 23.7, 26.8, 30.5, 30,8 (intense), 30.9, 33.1, 34.4 ($(CH_2)_9$), 62.4 (C-6), 62.9 (C-6′), 71.5 (C-4′), 71.8 (C-4), 72.1 (CHOH), 73.1 (C-2), 73.6 (C-5′), 73.7 (C-3′), 73.9 (C-5), 74.6 (C-3), 76.8 (O-CH_2), 81.7 (C-2′), 93.3 (C-1′), 95.7 (C-1).

Second epimer. ^{1}H NMR (500 MHz, MeOD): δ (ppm) 0.85–0.88 (t, 3H, J = 7.0 Hz; CH_3); 1.20–1.50 (m, 18H, $(CH_2)_9$); 3.21–3.38 (m, 4H, H-2′, H-4, H-4′, OC*H_2*-b); 3.47 (dd, 1H, $J_{1,2} = 3.5$ Hz, $J_{2,3} = 9.7$ Hz; H-2); 3.59–3.92 (m, 10H, H-6′b, H-6b, C*H*OH, H-3, OC*H_2*-a, H-6a, H-6′a, H-5, H-5′, H-3′); 5.08 (d, 1H, H-1), 5.28 (d, 1H, $J_{1',2'} = 3.5$ Hz; H-1′); ^{13}C NMR (125 MHz, MeOD): δ (ppm) 14.5 (CH_3), 23.7, 26.6, 30.5, 30.8 (intense, 30,9, 33,1, 34.1 $(CH_2)_9$), 62.4 (C-6), 62.7 (C-6′), 71.6 (C-4′), 71.8 (C-4), 72.1 (CHOH), 73.1 (C2), 73.6 (C-5′), 73.6 (C-3′), 73.9 (C-5), 74.6 (C-3), 76.9 (O-CH_2), 82.1 (C-2′), 93.3 (C-1′), 95.7 (C-1).

2.6.1.1.2. 3-O-(β-Hydroxydodecyl) trehalose. ^{1}H NMR (500 MHz, MeOD): δ (ppm) 0.84–0.89 (t, 3H, J = 7.0 Hz, CH_3); 1.20–1.50 (m, 18H, $(CH_2)_9$); 3.30 (t, 1H, $J_{3,4} = J_{4,5} = 9.7$ Hz; H-4); 3.36–3.44 (2 pseudo t, 1H, $J_{3',4'} = J_{4',5'} = 9.7$ Hz; H-4′); 3.47 (dd; 1H; $J_{1,2} = 3,8$ Hz, $J_{2,3} = 9.8$ Hz; H-2); 3.50–3.60 (2dd, 1H, H-2′); 3.58–3.63 (dd, 1H; $J_{Ha,Hb} = 10.5$ Hz, $J_{Hb,CHOH} = 7.8$ Hz; OC*H_2*b); 3.63–3.68 (m, 3H, H-6b, H-6′b, H-3′); 3.72–3.82 (m, 6H, H-3, H-5, H-5′, H-6a, H-6b, C*H*OH); 3.84–3.89 (2dd, 1H; $J_{Ha,CHOH} = 3.5$ Hz; OC*H_2*a); 5.09 (d, 2H, H-1, H-1′); ^{13}C NMR (125 MHz, MeOD): δ (ppm) 14.5 (CH_3); 23.8, 26.7/26.8 (d), 30.5, 30.7 (intense), 30.9, 33.1, 34.2/34.3 (d) ($(CH_2)_9$), 62.4 (C-6), 62.6 (C-6′), 71.5 (C-4′), 71.9 (C-4), 72.3 (CHOH), 73.1 (C-2), 73.2 (C-2′), 73.8 (C-5), 73.8 (C-5′), 74.5 (C-3), 78.5 (O–CH_2), 83.9 (d) (C-3′), 94.9 (C-1′, C-1).

2.6.1.1.3. 4-O-(2-Hydroxydodecyl) trehalose. ^{1}H NMR (500 MHz, MeOD): δ (ppm) 0.84–0.89 (t, 3H, J = 6.9 Hz; CH_3); 1.20–1.50 (m, 18H, $(CH_2)_9$); 3.22–3.32 (m, 2H, H-4, H-4′); 3.43 (dd, 1H, $J_{1,2} = 3.8$ Hz, $J_{2,3} = 9.8$ Hz; H-2); 3.47 (dd, 1H, $J_{1',2'} = 3.8$ Hz, $J_{2',3'} = 9.8$ Hz, H-2′); 3.49–3.53 (dd; 0.5H; $J_{Hb,CHOH} = 7.8$ Hz, $J_{Ha,Hb} = 10.4$ Hz; OC*H_2*b (first epimer); 3.58–3.84 (m, 9.5 H, H-6a, H-6b, H-6′a, H-6′b, H-5, H-5′, H-3, C*H*OH, OC*H_2* a (α/β), OC*H_2*b (second epimer); 3.84-3.94 (two pseudo t, 1H, $J_{2',3'} = J_{3',4'} = 9.4$ Hz; H-3′); 5.06 (d, 1H, $J_{1',2'} = 3.8$ Hz; H-1′); 5.08 (d, 1H, $J_{1,2} = 3.8$ Hz, H-1); ^{13}C NMR (125 MHz, MeOD): δ (ppm) 14.5 (CH_3); 23.7, 26.6/26.8 (d), 30.5, 30.8 (intense), 30.9, 33.1, 34.3 ($(CH_2)_9$), 62.0 (C-6′), 62.6 (C-6), 71.8 (CHOH β), 71.8 (C-4), 72.5 (CHOH α), 72.8 (C-5′), 73.1 (C-2), 73.2 (C-2′), 73.8 (C-5), 74.4 (d) (C-3′), 74.4 (C-3), 77.8, 78.4 (O-CH_2), 80.1, 80.7 (C-4′), 94.9, 95.0 (C-1′, C-1).

2.6.1.1.4. 6-O-(2-Hydroxydodecyl) trehalose. ^{1}H NMR (500 MHz, MeOD): δ (ppm) 0,85–0,90 (t, 3H, $J = 6.9$ Hz, CH$_3$); 1.20–1.50 (m, 18H, (CH$_2$)$_9$); 3.28–3.50 (m, 6 H, H-4, H-4′, OC*H$_2$*, H-2, H-2′); 3,62–3,71 (m, 4H, H-6b, H-6′b, H-6′a, C*H*OH); 3.74–3.83 (m, 4H; H-6a, H-3, H-3′, H-5); 3.91–3.97 (m, 1H, H-5′); 5.05–5.09 (m, 2H, H-1, H-1′); ^{13}C NMR (125 MHz, MeOD): δ (ppm) 14.5 (CH$_3$), 23.7, 26.7 (d), 30.5, 30.8 (intense), 30.9, 33.0, 34.5/34.6 (d) ((CH$_2$)$_9$), 62.6 (C-6), 71.4 (d) (CHOH), 71.6 (d) (C-6′), 71.8 (C-4, C-4′), 72.6 (d) (C-5′), 73.1 (C-2, C-2′), 73.8 (C-5), 74.4 (C-3), 77.1 (d) (O-CH$_2$), 95.1 (d), 95.2 (d) (C-1′, C-1).

2.6.1.2. Di-O-(2-hydroxydodecyl)trehalose (5b) (mixture of regioisomers). ^{1}H NMR (300 MHz, MeOD) δ (ppm): 0.90 (t, $J = 6.8$ Hz, 6H, 2Me), 1.25–1.55 (m, 36H, 2 (CH$_2$)$_9$); 3.20–4.05 (m, 18H, C*H*OH, C*H$_2$*OH, OC*H$_2$*); 5.00–5.35 (m, 2H, H-1, H-1); SM-HR (FAB+): *m/z* calculated for C$_{36}$H$_{71}$O$_{13}$ [MH]$^+$: 711.4895. Found: 711.4899.

2.6.1.3. Tri-O-(2-hydroxydodecyl)trehalose (5c) (mixture of regioisomers). ^{1}H NMR (300 MHz, MeOD) δ (ppm): 0.90 (t, $J = 6.8$ Hz, 9H, 3Me); 1.25–1.55 (m, 48H, 3 (CH$_2$)$_9$); 3.20–4.05 (m, 21H, C*H*OH, C*H$_2$*OH, OC*H$_2$*); 5.00–5.35 (m, 2H, H-1, H-1′); SM-HR (FAB+): *m/z* calculated for C$_{48}$H$_{94}$O$_{14}$Na [MNa]$^+$: 917.6541. Found: 917.6540.

2.6.2. Characterization of 6a and b

Isomalt$^®$ is a mixture of 6-O-(α-D-glucopyranosyl)-D-sorbitol (6-GPS) and 1-O-(α-D-glucopyranosyl)-D-mannitol (1-GPM).

Mono-, dihydroxyalkylethers of isomalt$^®$ **6a** and **b** were separated over silica chromatography using an eluent CH$_2$Cl$_2$/MeOH/acétone/eau: 67/10/10/2,5. After freeze-drying, a white powder was obtained for **6a** and **6b**.

2.6.2.1. Mono-O-(2-hydroxydodecyl) isomalt$^®$ (6a) (mixture of isomers). ^{1}H NMR (300 MHz, MeOD) δ (ppm): 0.86–0.95 (t, 3H, $J = 6.7$ Hz, Me); 1.23–1.53 (m, 18H, (CH$_2$)$_9$); 3.25–4.05 (m, 17 H, C*H*OH, C*H$_2$*OH, OC*H$_2$*); 4.78–4.85 (m, 1H, H-1); SM-HR (FAB+): *m/z* calculated for C$_{24}$H$_{49}$O$_{12}$ [MH]$^+$: 529.3224. Found: 529.3226; Elemental analysis: calc. for C$_{24}$H$_{48}$O$_{12}$ (with 1.6H$_2$O): C, 51.71; H, 9.26; O, 39.03; found: C, 51.75; H, 9.30; O, 39.01

2.6.2.2. Di-O-(2-hydroxydodecyl) isomalt$^®$ (6b) (mixture of isomers). ^{1}H NMR (300 MHz, MeOD) δ (ppm) 0.90 (t, $J = 6.7$ Hz, 6H, 2Me); 1.23–1.55 (m, 36H, 2 (CH$_2$)$_9$); 3.25–4.05 (m, 20H, C*H*OH, C*H$_2$*OH, OC*H$_2$*); 4.78–4.90 (m, 1H, H-1), SM-HR (FAB+) *m/z* calculated for C$_{36}$H$_{73}$O$_{13}$ [M+2H]$^+$: 714.5029. Found: 714.5033.

3. Results and discussion

3.1. Influence of the catalytic surface lipophilicity

A good control of the hydrophilic–lipophilic balance of the catalyst is known to be an important parameter having influ-
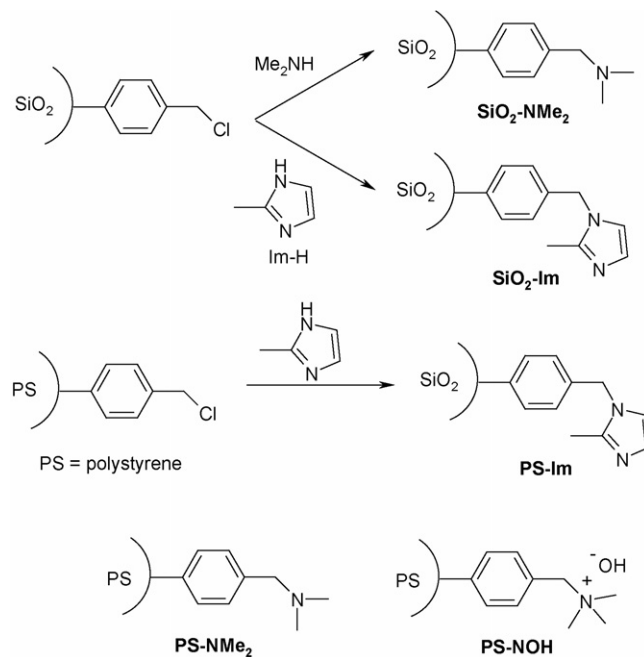
Scheme 2. Solid basic catalysts investigated.

ence on the outcome of polyol esterification, notably in terms of degree of substitution [6,8]. In this study, five different kinds of solid basic catalysts were investigated: SiO$_2$–NMe$_2$, SiO$_2$–Im, PS–Im, PS–NMe$_2$, and PS–NOH (Scheme 2). The two solid catalysts SiO$_2$–NMe$_2$ and SiO$_2$–Im were prepared by direct grafting of dimethylamine and 2-methylimidazole over a chlorobenzyl silica (chlorine content: 2.5 mmol/g) following by a washing with a basic solution of guanidine in acetonitrile in order to remove the quaternary ammonium salts formed as side products (see Section 2). Elemental analyses revealed an amino content of 1.5 mmol/g and 1.3 mmol/g for SiO$_2$–NMe$_2$ and SiO$_2$–Im, respectively. PS–Im (PS: polystyrene framework) was prepared by direct grafting of 2-methylimidazole over a Merrifield's resin (chlorine content: 2.6 mmol/g). Elemental analyses indicated a loading of 2.2 mmol of methylimidazole group per gram of PS–Im which corresponds to a chlorine substitution of 85%. PS–NMe$_2$ and PS–NOH were kindly provided by Rohm and Hass and exhibit a respective amino group content of 4.7 and 4.4 mmol/g.

The catalytic activities of these five solid catalysts were studied in the etherification of sucrose with 1,2-epoxydodecane. Typically, sucrose (10 mmol) was mixed with 1,2-epoxydodecane (2.5 mmol) in DMSO (5 mL). The reaction mixture was then heated at 110 °C before addition of the solid catalyst (0.5 equiv. of supported catalytic sites). Surprisingly, starting from SiO$_2$–NMe$_2$ and SiO$_2$–Im very poor yields (<9%) into sucrose hydroxyalkylethers were obtained, (Fig. 1; Table 1, entries 1–2) and the epoxydodecane was totally degraded. It is noteworthy that this degradation of the epoxydodecane is a thermal reaction since the presence of a solid basic catalyst does not increase the epoxide degradation rate. We assume that this low reactivity of SiO$_2$–NMe$_2$ and SiO$_2$–Im was related to their high hydrophilicity. Indeed, in both cases, amino groups are not basic
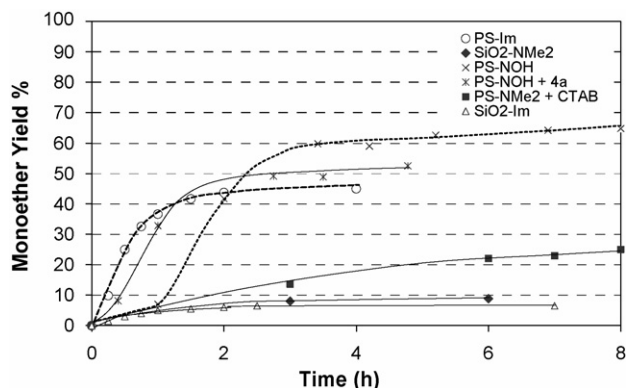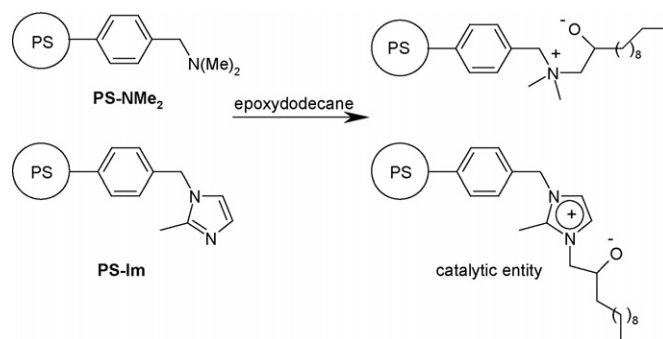
Fig. 1. Catalytic activity of SiO_2–NMe_2, PS–NMe_2, PS–Im and PS–NOH (0.5 equiv. or 11 wt.%).

Scheme 3. Formation of the catalytic entity.

enough to directly deprotonate the sucrose (pK_a between 11 and 13). For this reason, in the case of weakly basic tertiary amines, it is well established that the first step of the catalytic mechanism is the nucleophilic addition of the amino group to the epoxide leading to the formation of a strongly basic quaternary ammonium salt responsible for the catalysis. However, as the epoxydodecane is highly lipophilic, its adsorption to the siliceous surface of SiO_2–NMe_2 and SiO_2–Im is very slow. Consequently, the thermal epoxide degradation was in this case more rapid than its reaction with sucrose explaining the low formation of sucrose ethers when starting from siliceous materials. It is interesting to note that assistance of cetyltrimethylammonium bromide (CTAB) as phase transfer agent or a silylation of the free silanol groups of SiO_2–NMe_2 and SiO_2–Im, with the aim of decreasing the hydrophilicity of the catalyst, do not lead to an improvement of the sucrose hydroxyalkylethers yields indicating that the silica network is still too hydrophilic to allow a rapid adsorption of the epoxydodecane to the catalytic sites.

Based on this assumption, the hydrophilic silica framework was replaced by a lipophilic polystyrene network. In the case of the PS–NMe_2 solid catalyst, sucrose hydroxyalkylethers were still produced with poor yield (15%) (Table 1, entry 3) along with an important degradation of the epoxydodecane. Indeed, nucleophilic addition of the grafted amino groups to the epoxy-

dodecane, requisite step for the production of the catalytic entity, leads to a strong increase of the lipophilicity of PS–NMe_2 surface. Consequently, in this case, the adsorption of sucrose was now considerably limited allowing therefore a competitive thermal degradation of the epoxide. However, whereas addition of a phase transfer agent with siliceous catalysts had no positive impact on the sucrose ethers yield, addition of 10 mol% of CTAB to PS–NMe_2 made easier the diffusion of sucrose to the catalyst surface allowing thus the production of sucrose ethers with yield higher than 25% yield (Table 1; entry 5). This result shows that the PS–NMe_2 solid catalyst exhibits a more appropriated hydrophilic–lipophilic balance than SiO_2–NMe_2 for the catalytic etherification of sucrose with fatty epoxydodecane. Remarkably, PS–Im solid catalyst exhibits a greater catalytic activity than PS–NMe_2 since, without assistance of a phase transfer agent, sucrose monohydroxyalkylethers were produced with more than 44% yield in less than 4 h (Table 1, entry 4). This particular behavior of PS–Im can be first explained by its higher basicity. Indeed, after formation of the catalytic entity, the delocalization of the positive charge in the imidazole moiety makes more basic the resulting alcoholate accelerating thus the deprotonation rate of sucrose (Scheme 3). Secondly, addition of 10 mol% of CTAB had no impact as well as on the reaction rate and the reaction yield. This result clearly indicates that the PS–Im catalyst has a more appropriated hydrophilic–lipophilic balance than PS–NMe_2 for the presented reaction and can acts as

Table 1
Synthesis of sucrose hydroxyalkylethers over basic solid catalysts[a]

Entry	Catalyst	Time (h)	Monoethers (%)[b]	Diethers (%)[b]	Others[c]
1	SiO_2–NMe_2	4	4a (9)	4a not detected	91
2	SiO_2–Im	4	4a (6)	4a not detected	94
3	PS–NMe_2	6	4a (15)	4a not detected	81
4	PS–Im	4	4a (44)	4a not detected	56
5	PS–NMe_2/CTAB	8	4a (25)	4a not detected	75
6	PS–NOH	5	4a (62)	4a (6)	32
7	PS–NOH[d]	3	4a (50)	4a (10)	40
8	PS–NOH[e]	8	4a (39)	4a not detected	61
9	PS–NOH[f]	6	4a (57)	4a (2)	41

[a] Unprotected sucrose (10 mmol), 1,2-epoxydodecane (2.5 mmol), 5 mL of DMSO, 110 °C, 0.5 equiv. of solid catalysts.
[b] Molar yields were calculated by HPLC.
[c] Epoxide degradation products: dodecanediol (quantified by HPLC) + oligomers/polymers not detected by HPLC (quantity determined by the carbon balance).
[d] Addition of 10 mol% of 4a.
[e] Sucrose solution of 1 M.
[f] Sucrose solution of 3 M.

phase transfer agent allowing a faster diffusion of both reagents to the catalytic surface. However, starting from PS–Im catalyst, a maximum yield of 44% into sucrose ethers was reached. This maximum yield is linked to the unavoidable consumption of the epoxydodecane by the catalyst in order to generate the catalytic entity. Indeed, at the end of the reaction, elemental analyses of the recovered PS–Im solid catalyst confirmed an important increase of the percent ratio C/N from 12.4 to 17.3. The influence of the catalyst amount on the reaction yield will be discussed in the next section.

In order to reach higher yield in **4**, it occurred to us that a solid catalyst, with an appropriated hydrophilic–lipophilic balance, able to directly deprotonate sucrose will be a much more convenient solid catalyst.

When the PS–NOH solid catalyst was used, the first step of the catalytic process is now the direct deprotonation of sucrose by the heterogeneized hydroxide group. The resulting catalytic intermediate exhibits then highly hydrophilic sucrate catalytic sites grafted over a lipophilic framework. As expected, in absence of CTAB, this solid catalyst was able to limit the epoxydodecane degradation and afforded more than 68% yield into sucrose hydroxyalkylethers with 62% selectivity to mono-hydroxyalkylether derivative **4a** (Table 1, entry 6). Remarkably, it is noteworthy that in experiment with the PS–NOH solid catalyst, the initial reaction rate was quite slow (Fig. 1). However, after formation of about 10 mol% of sucrose monohydroxy-alkylethers, an important increase of the reaction rate occurred (Fig. 1). This can be attributed to the surfactant properties of derivative **4** [9]. Indeed, this latter can act as a phase transfer agent allowing a better diffusion of the reagents to the catalytic surface. This effect was also illustrated when 10 mol% of sucrose monohydroxyalkylether (**4a**) was initially added with the PS–NOH catalyst. Remarkably, in this case, the reaction more rapidly produces ethers with almost no more sigmoidal curve (Fig. 1). However, this increase of the reaction rate did not allow to reduce the undesirable epoxide degradation, showing that the presence of sucrose monohydroxyalkylether (**4a**) as phase transfer agent made also easier the contact of the epoxydodecane with the grafted ammonium hydroxide groups favouring thus its hydrolysis and/or its polymerization as soon as the beginning of the catalytic process (Table 1, entry 7).

From the results presented in Fig. 1, it appears that the PS–NOH solid catalyst exhibits a less appropriated hydrophilic–lipophilic balance than the PS–Im solid catalyst since PS–NOH catalyst is initially less active. However, thanks to the surfactant properties of **4a** and as almost no consumption of the epoxydodecane occurred over the grafted hydroxide groups, the PS–NOH allowed us to obtain the best yield in sucrose monohydroxyalkylethers.

3.2. Influence of the sucrose concentration

We found that a starting sucrose concentration of 2 M was the optimum one to obtain the best yield into sucrose ethers. Using more diluted solutions (1 M in sucrose), the catalytic reaction rate decreased and compounds **4a** were produced with only 39% yield (Table 1, entry 8) with faster epoxide

degradation. Reversely, using a 3 M sucrose concentration, the DMSO phase was totally saturated by the sucrose and the 1,2-epoxydodecane became sparingly miscible with the reaction mixture. Consequently, in this case, the catalytic reaction rate was also decreased and ethers **4a** were only produced with 57% yield along with 41% of epoxydodecane degradation products (Table 1, entry 9).

3.3. Influence of the catalyst amount

In order to limit the thermal degradation of the epoxydode-cane, the impact of the amount of solid catalyst on the sucrose ethers yield was investigated (Fig. 2). Yield presented in Fig. 2 are given at total conversion of the epoxydodecane.

When 0.1 equiv. of PS–Im or PS–NOH solid catalysts was used, very poor yields into sucrose hydroxyalkylethers were obtained (10%). Indeed, in this case, the thermal degradation of the epoxide was faster than the catalytic process. Surprisingly, whereas with 0.2 equiv. of solid catalyst we logically expected to double the yield into sucrose hydroxyalkylethers, more than 33% yield into **4** was obtained. This net increase of the sucrose ethers yields is due to the amphiphilic properties of PS–Im catalyst and to the greater production of sucrose monohydroxyalkylethers in the case of the PS–NOH solid catalyst. Indeed, as described above, when derivative **4** or PS–Im solid catalyst are in suffi-cient quantity, they act as phase transfer agents and homogenize the reaction mixture making easier the diffusion of the reagents to the catalytic surfaces and favouring the production of sucrose ethers to the detriment of the epoxide degradation.

With 0.3 equiv. of solid catalyst, the PS–NOH solid catalyst was more efficient than PS–Im and led to the better yield (55%) of sucrose ethers. This lower yield obtained with PS–Im is due to the important consumption of the epoxide by the solid catalyst in order to generate the catalytic entity. Between 0.3 and 0.5 equiv. of PS–Im solid catalyst no increase of the sucrose ethers yield was observed. Indeed, with 0.3 and 0.5 equiv. of PS–Im, only 44% yield into **4** was obtained. However, if we take into account the epoxide consumption by the solid catalyst, the sucrose ethers selectivity of the process is more important with 0.5 equiv. of PS–Im (88%) than with 0.3 equiv. (63%). In the case of 0.5 equiv. of PS–NOH solid catalyst, the yield into **4** raised to 68% to the detriment of the thermal epoxide degradation.
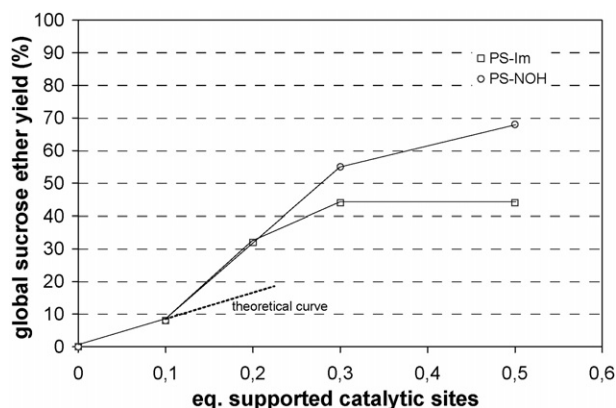

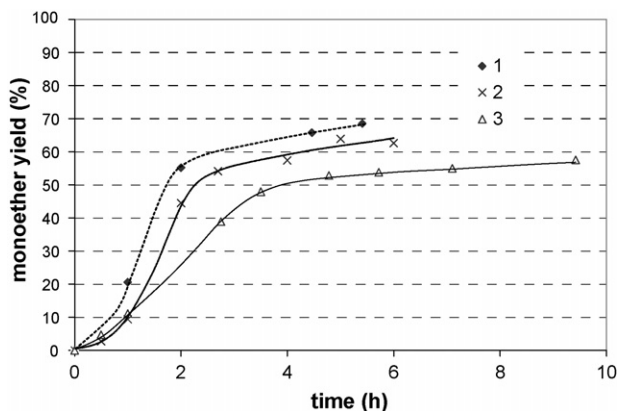Fig. 2. Influence of the catalyst amount.

Fig. 3. monoethers synthesis over 15 wt.% of PS–NOH catalyst.

From this study, it clearly appears that the thermal epoxide degradation is not a negligible side reaction and constrains us to use an important amount of solid catalyst in order to favour the production of sucrose ethers.

3.4. Extension of the catalytic procedure to trehalose and isomalt

Based on this study, we extended our catalytic process to trehalose and isomalt® which are two other disaccharides issued from renewable feedstock. As solid catalyst, we focussed our researches towards the use of the PS–NOH catalyst which allowed to obtain the best yield into sucrose ethers. As in the case of sucrose, 10 mmol of disaccharide (**2** and **3**) were mixed with 1,2-epoxydodecane (2.5 mmol) in DMSO (5 mL). The reaction mixture was then heated at 110 °C before addition of 15 wt.% of dry PS–NOH catalyst. As expected, the PS–NOH heterogeneous catalyst appeared to be a very versatile catalyst since isomalt® ethers **6** were produced with more than 68% yield and a respective selectivity into monoethers **6a** of 65% (Fig. 3; Table 2, entry 2). As what was observed in the case of sucrose, the reaction rate considerably increased after formation of about 10 mol% of isomalt® monohydroxyalkylethers (**6a**) (Fig. 3).

Surprisingly, starting from trehalose, ethers of trehalose **5** were produced in slightly lower yield (60%) but still with a high

monoether **5a** selectivity of 57% (Fig. 3; Table 2, entry 3). In this case, the reaction rate was slower leading to a more important epoxide degradation.

It is worth noting that this particular behavior of trehalose was not observed using potassium hydroxide as homogeneous catalyst (Table 2, entries 4–6). These results clearly illustrate that the differences of reactivity observed between **1**, **2** and **3** are related to variations in their ability to approach the grafted catalytic sites.

In the case of sucrose, intramolecular hydrogen bonds make the OH group at position 2 more acidic than those usually observed for other disaccharides and consequently sucrose reacted faster than **2** and **3** [2d,10]. Isomalt® exhibits a lower OH function reactivity compared to sucrose, but this is compensated by an increased flexibility due to the linkage of the glucose moiety with a linear polyol chain. Consequently, due to weakest steric interaction with the catalytic surface, this latter more easily diffuses inside the polystyrene network. Conversely, trehalose, with its two linked glucose units and the weaker OH group reactivity, leads to a slower reaction.

3.5. Structural aspects

On the regiochemical point of view, the reaction was studied in details by HPLC and NMR for the case of trehalose for comparison with sucrose (isomalt®, being a mixture of two epimers, leads to mixtures of products which are too complex to be studied). Trehalose structurally differs from sucrose by the presence of a α glucosyl moiety instead of a β fructosyl linked to the α glucopyranosidic ring. This symmetrical disaccharide can therefore provide only four sites for monoetherification (each regioisomer being actually a mixture of two epimers at the hydroxydodecanoyl part). It was therefore interesting to compare the distribution of the various regioisomers on the glucose moiety for both sucrose and trehalose. As seen in Table 3, the distribution of regiosomers differs significantly essentially because of the higher reactivity of the OH-2 of sucrose. If only the relative proportions of ethers at OH-3, -4 and -6 position are compared, then similar ratios are observed. This provides another proof for the preeminent reactivity at OH-2 of sucrose, confirming other observations in preparative, spectroscopic or theoretical studies [2d,9].

Table 2
Extension of the catalytic process to trehalose and isomalt®

Entry	Disaccharide[a]	Catalyst	Time (h)	Monoethers (%)[b]	Diethers (%)[b]	Others[c]
1	**1**	PS–NOH	6	**4a** (68)	**4b** (10)	22
2	**2**	PS–NOH	5	**5a** (65)	**5b** (3)	32
3	**3**	PS–NOH	5	**6a** (57)	**6b** (3)	40
4	**1**[d]	KOH	10	**4a** (58)	**4b** (22)	20
5	**2**[d]	KOH	10	**5a** (58)	**5b** (22)	20
6	**3**[d]	KOH	10	**6a** (54)	**6b** (26)	20

[a] Unprotected disaccharide (10 mmol), 1,2-epoxydodecane (2.5 mmol), 5 mL of DMSO, 110 °C, 15 wt.% of solid catalysts.

[b] Molar yields were calculated by HPLC.

[c] Epoxide degradation products: dodecanediol (quantified by HPLC) + oligomers/polymers not detected by HPLC (quantity determined by the carbon balance).

[d] Catalytic process performed starting from a disaccharide/epoxydodecane molar ratio of 2.

Table 3

Proportions of regioisomers in monohydroxyalkylethers of trehalose, sucrose, and the glucosyl part of sucrose

OH groups	Position[a]							
	3	4	6	2	3′	1′	4′	6′
All (8) positions in **4a**	1%	5%	7%	41%	14%	25%	4%	4%
All (4) positions in **5a**	9%	30%	37%	24%	–	–	–	–
The four positions of the glucose moiety of **4a**	2%	9%	13%	76%	–	–	–	–
Positions 3, 4, 6 of **5a**	12%	40%	48%	–	–	–	–	–
Positions 3, 4, 6 of **4a**	8%	38%	54%	–	–	–	–	–

[a] The regioisomer distribution was determined by HPLC and each regioisomer was identified by NMR.

3.6. Catalytic process in water and DMSO/water mixtures

Even if DMSO can be considered as one of the most acceptable dipolar aprotic solvents in terms of toxicity, the reaction was also explored in water which is definitely environmentally friendlier.

Using the same experimental conditions except replacing DMSO by water, lower yield of sucrose monohydroxyalkylethers (**4a**) was obtained (14%, Table 4, entry 1) with important concomitant degradation of the epoxide (86%). This poor reactivity was mainly due to the non-miscibility of the epoxydodecane in water. In order to favour a better contact between sucrose, 1,2-epoxydodecane and the PS–NOH catalyst, a phase transfer agent was added in the reaction mixture. Addition of 10 mol% of CTAB immediately started the catalytic process and sucroethers **4** were produced with 78% yield, to the detriment of the epoxide degradation (Table 3, entry 2). Surprisingly, even with a molar ratio sucrose/epoxide of 4, the selectivity towards sucrose monosubstituted ethers **4a** was much lower (36%) than in DMSO (62%) since in water **4a** derivative

was produced along with more than 42% of sucrose dihydroxyalkylethers (**4b**) (Table 4, entry 2). This change of selectivity was essentially due to strong hydrophilic interaction. Indeed, even with the use of CTAB, sucrose monohydroxyalkylethers (**4a**) are much less soluble in water than in DMSO and consequently, these latter stronger interact with 1,2-epoxydodecane. On the other hand, this result also indicates that, in pure water, the PS–NOH catalyst stronger interacts with the epoxydodecane phase than with the aqueous solution of sucrose enhancing thus the production of polysubstituted products. As a perfect illustration, an increase of the sucrose/epoxide molar ratio from 4 to 8 did not significantly improve the selectivity of the reaction confirming the greater affinity of the PS–NOH solid catalyst for the fatty derivatives than for the sucrose phase (Table 4, entry 3).

Starting from trehalose and isomalt®, ethers of disaccharides were obtained in lower yield than in the case of sucrose since ethers of trehalose and isomalt® were respectively produced with 45 and 47% yield and a respective **2a**, **3a** monoether selectivity of 22 and 26% (Table 4, entries 4 and 5). As described above in the case of DMSO, trehalose was less reactive than sucrose because of steric interaction and lower OH function reactivity. In the case of isomalt®, the presence of one more hydroxyl group on the sugar moiety makes this latter more soluble in water and consequently the lipophilic interactions between isomalt®, 1,2-epoxydodecane and the PS–NOH solid catalyst were increased explaining the poorer reactivity observed when starting from **3**.

When CTAB was replaced by the amphiphilic sucrose monohydroxyalkylethers (**4a**), a slower reaction rate was observed (Table 4, entry 6). This poorer reactivity observed in water when using **4a** instead of CTAB as phase transfer agent was directly linked to its weaker amphiphilic properties making still difficult the contact between the reagents and the PS–NOH catalyst (Table 4, entry 6).

Table 4

Influence of water on the reaction selectivity

Entry	Disaccharide[a]	Additive[b]	DMSO (%)	Water (%)	Time (h)	Monoethers (%)[c]	Diethers (%)[c]	Others[d]
1	**1**	–	0	100	24	**4a** (14)	**4b** and **c** (0)	86
2	**1**	CTAB	0	100	7	**4a** (36)	**4b** and **c** (42)	22
3	**1**[e]	CTAB	0	100	7	**4a** (43)	**4b** and **c** (34)	23[f]
4	**2**	CTAB	0	100	20	**5a** (22)	**4b** and **c** (23)	55
5	**3**	CTAB	0	100	16	**5b** (26)	**4b** and **c** (21)	53
6	**1**	**4a**	0	100	18	**4a** (34)	**4b** and **c** (23)	43[f]
7	**1**	–	100	0	5	**4a** (62)	**4b** and **c** (6)	32
8	**1**	–	50	50	22	**4a** (28)	**4b** and **c** (12)	60
9	**1**	CTAB	50	50	5	**4a** (47)	**4b** and **c** (38)	15
10	**1**	–	70	30	10	**4a** (45)	**4b** and **c** (8)	47
11	**1**	CTAB	70	30	5	**4a** (58)	**4b** and **c** (29)	13
12	**1**	CTAB	90	10	5	**4a** (60)	**4b** and **c** (21)	19

[a] Unprotected disaccharide (10 mmol), 1,2-epoxydodecane (2.5 mmol), 5 mL of solvent, 100 °C, 15 wt.% of dry PS–NOH catalyst.

[b] 10 mol%.

[c] Molar yields were calculated by HPLC.

[d] Products resulting from the polyetherification of sucrose and from the epoxide degradation.

[e] Sucrose/1,2-epoxydodecane molar ratio of 8.

[f] Contain 5% of remaining 1,2-epoxydodecane.

3.7. Catalyst stability

Remarkably, we found that the PS–NOH catalyst was much more stable in water than in pure DMSO. Indeed, in the case of DMSO we observed a strong deactivation of the solid catalyst during the catalytic process limiting thus the possible recycling of the solid catalyst. In the case of water, the PS–NOH catalyst could be recycled at least five times without noticeable degradation. Consequently, with the aim of avoiding the polysubstitution of sucrose while keeping a great stability of the PS–NOH catalyst during the reaction, mixtures of DMSO and water were used as solvent.

In the case of a 1:1 DMSO–H$_2$O mixture, the global yield of sucroethers **4** dramatically dropped from 68% (in DMSO) to 40% (Table 4, entry 8) mainly due to the greater affinity of the solid catalyst for the fatty derivatives. As in the case of pure water, addition of 10 mol% of CTAB favored the sucroethers **4** production and these latter were now obtained with more than 85% yield (Table 4, entry 9). As a consequence, contrary to what was previously obtained in pure water, the sucrose monohydroxyalkylethers (**4a**) yield was raised from 14% (in pure water) to 47% in a mixture DMSO–H$_2$O 1:1 (Table 4, entry 9).

In a 7:3 DMSO–H$_2$O mixture, sucroethers **4** were produced, in absence of CTAB, with 53% yield (Table 4, entry 10), whereas with assistance of 10 mol% of CTAB, the production of sucroethers **4** raised to more than 87% yield with a higher selectivity into sucrose monohydroxyalkylethers (**4a**) of 58% (Table 4, entry 11). Interestingly, in aqueous solution, this 7:3 DMSO–water ratio appeared to be the best composition to obtain the higher yields into the desired monoethers **4a**. Indeed, with lower loading of water, no significant improvement of the sucrose monohydroxyalkylethers (**4a**) yield was observed (Table 4, entry 12).

As expected, the replacement of 30% of DMSO by water allowed to obtain **4a** with similar yield than in the case of DMSO and made the PS–NOH catalyst much more stable. Therefore, at the end of the reaction, the catalyst was recovered by filtration and, after washing with a DMSO–H$_2$O 7/3 mixture, reused at least 4 times without notable change of reactivity pushing forward the key contribution of water regarding the stability of the solid catalyst.

3.8. Physicochemical investigations

A series of simple experiments were achieved with the goal of giving preliminary clues concerning the physicochemical behavior of the newly prepared amphiphilic materials.

First, the critical miscellar concentration (CMC) of the monoethers **4a**, **5a** and **6a** were measured by tensiometry. As shown in Fig. 2, no significant difference of CMC was observed between **4a** and **5a** which both exhibit a CMC of 1 mmol/L.

Monohydroxyalkylethers of isomalt® (**6a**) exhibited a higher CMC of 2.5 mmol/L. This increase of the CMC value was attributed to the presence of one more hydroxyl group on the isomalt® molecule increasing thus the hydrophilic nature of **6a** and its solubility in water, therefore delaying the formation of
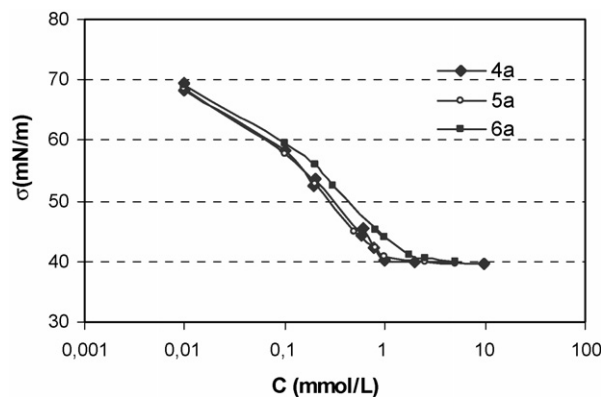

Fig. 4. Surface tension of **4a**, **5a** and **6a**.

miscellar arrangements compared to what was observed with **4a** and **5a** (Fig. 4).

Then the diffusion behavior of sucrose monohydroxyalkylethers (**4a**) was estimated by PGSE–NMR in D$_2$O and compared to the standard sucrose esters having fatty chains in C$_{10}$ and C$_{12}$ [11]. As represented in Fig. 3, this spectroscopic technique confirmed the CMC value previously obtained for **4a** (1 mmol/L). The CMC of sucrose monohydroxyalkylethers (**4a**) is intermediate between that of C$_{10}$ and C$_{12}$ sucrose ester. This result comes from the difference of structure between sucrose esters compared to the ethers studied here, for which, the hydroxyalkyl linkage brings a supplementary hydroxyl group which increases the hydrophily of the polar moiety and shortens in the same time the fatty chain of one CH$_2$ group (Fig. 5).

Finally, foaming properties were estimated by the Ross–Miles method under the simplified procedure described by Garafolakis and Murray consisting in measuring the foam height and stability after consistent agitation [12]. The monohydroxyalkylethers **4a**, **5a** and **6a** were compared to a series of classical surfactants (Sodium dodecylsulfate (SDS), Polyethoxylated fatty alcohol (Brij35), C$_{12}$-Alkylpolyglucoside (APG) and C$_{12}$-sucroester).

As shown in Fig. 4, the monohydroxyalkylethers **4a**, **5a** and **6a** exhibit, at 1 mg/mL, foaming properties in a similar range than commercialized surfactants such as SDS or sucroesters. Sucrose monohydroxyalkylethers **4a** can be easily mixed, with-
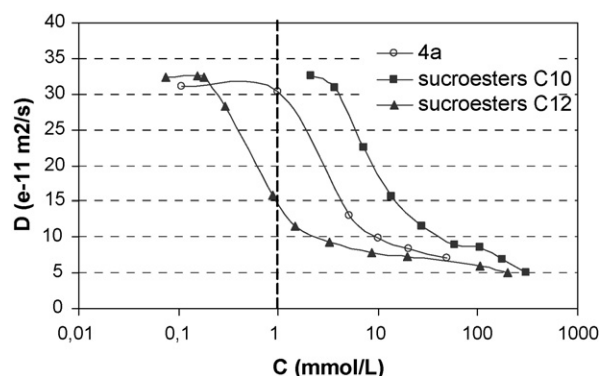

Fig. 5. Estimation of the diffusion behavior of **4a** by PGSE–NMR investigation and comparison to C10 and C12 sucroesters.
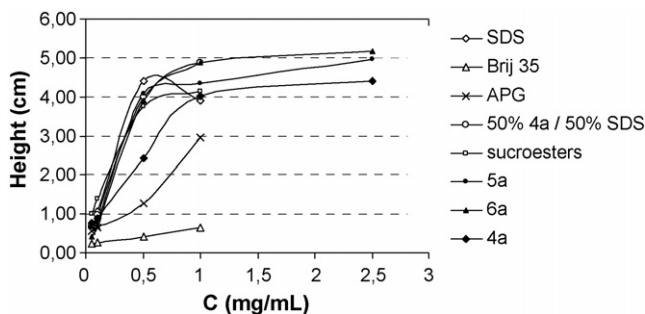
Fig. 6. Comparison of the foaming properties of **4a**, **5a** and **6a** with known non-ionic surfactants.

out affecting their foaming properties, with other surfactants such as SDS pushing forward the great versatility of the newly prepared fatty ethers (Fig. 6).

Although globally behaving in a similar manner, differences between **4a**, **5a** and **6a** were observed. For the initial foam height, sucrose monohydroxyalkylethers (**4a**) exhibited significantly lower values (ca. 60%) compared to isomalt® ethers **5a** and trehalose ethers **6a** at a concentration of 0.5 mg/mL, but this difference decreased significantly upon increasing the concentration at 1 mg/mL. Concerning the foam stability (data not shown), at 0.5 mg/mL, same values were measured for **4a**, **5a** or **6a** (only 4% of the initial foam collapsed after 1 h of decantation). At 1 mg/mL, **5a** and **6a** exhibited greater foam stability than **4a** (80% of the initial foam collapsed for **4a** whereas less than 30% for **5a** and **6a**). A hypothesis is that these variations could be related with the fact that the studied compounds are mixtures of isomers (regioisomers on all possible OH groups and epimers at the hydroxyalkyl linkage). Variations of foaming properties due to substrate heterogeneity have already been reported in the literature [13]. Here, the specific structures found in the regioisomeric distribution of sucrose ethers **4a** have significantly different conformations depending where the fatty chains is attached on the disaccharidic backbone. Previous work showed that major isomers are positioned on O-2 and O-1' since both are involved in the hydrogen bonding network which connects both moieties of the disaccharide and therefore have specific influence on the conformation [7]. This resulted in variations of the thermotropic behaviour [14]. Also, variations in the solution properties, observed by the diffusion behaviour, were recently reported for different regioisomers of sucrose esters [11].

4. Conclusion

The catalytic etherification of sucrose with 1,2-epoxydodecane is closely governed by hydrophilic–lipophilic interactions. According to the support solid over which are grafted the basic catalytic sites, different yields into disaccharide ethers were obtained. Siliceous materials are too hydrophilic and prevent the rapid adsorption of the fatty epoxide to the catalytic sites. Consequently, in this case, the thermal epoxide degradation occurs more rapidly than the catalytic process and disaccharide ethers were consequently produced with poor yields. Using a lipophilic polystyrene

framework functionalized with dimethylamino groups, greater yields are obtained showing that this solid catalyst exhibits a more appropriated hydrophilic–lipophilic balance for the presented reaction. Best catalytic activity was obtained with the PS–Im catalyst which is a polystyrene functionalized with methylimidazole goups. Indeed, this solid basic catalyst exhibits an optimal hydrophilic–lipophilic catalytic surface allowing a rapid diffusion of both reagents to the catalytic sites. Hydroxide groups immobilized over a polystyrene framework (PS–NOH) is initially less active than PS–Im but allow to obtain best yields into disaccharide ethers since no consumption of the epoxide was necessary to generate the catalytic species.

In the presence of water, more than 87% yield into sucrose ethers were still obtained and we found that the PS–NOH solid catalyst was much more stable than in pure DMSO allowing the reusing of the catalyst without change of activity, stability and selectivity affording a greener process. At the end of the reaction, the PS–NOH catalyst was easily recovered by filtration avoiding thus the neutralization step and consequently the side production of salts making of this route a more environmentally friendlier procedure than those usually reported in the disaccharide chemistry. The regioselectivity of the reaction was fully investigated by HPLC and NMR analyses and clearly evidenced the higher reactivity of the OH-2 of sucrose compared to other disaccharides. Preliminary studies regarding the surfactant properties of newly prepared amphiphilic molecules were investigated (CMC, foaming properties) and revealed that monohydroxyalkylethers of sucrose, trehalose and isomalt® exhibited similar foaming properties than commercialized non-ionic surfactants such as APG or sucroesters, with a very high foam stability.

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