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Synthesis and Characterization of a New Organocatalytic Biosourced Surfactant

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Abstract: This article describes the synthesis of a new bio-based organocatalytic surfactant. The nine steps of the synthesis were optimized, fully respecting the principles of green chemistry. The surfactant aspect was then evaluated with the use of tensiometric studies. The molecular organization of the surfactant in vesicles in an aqueous medium was characterized by Dynamic Light Scattering (DLS) and confirmed using Density Functional Theory (DFT) modelling.

Keywords: surfactant; green chemistry; bolaform

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1. Introduction

Since the advent of green chemistry [1], an important improvement has taken place with the substitution of petrol-based chemicals with bio-sourced ones [2] Additionally, in order to respect the principles of green chemistry [3–5] the replacement of organic toxic compounds by less (or non) toxic compounds has gained momentum and thus became a crucial feature. In organic synthesis, the solvent is the chemical compound which represents the largest proportion of the process. For instance, it represents 80% *w/w* of the total of the compounds used in a process in the pharmaceutical industry [6]. As a replacement for the commonly used toxic organic compounds, new "green" solvents have been developed such as 2-MeTHF, polyethylenglycol, ionic liquids or supercritical fluids [SCFs] [7–10]. However, the optimal solution is the use of water as a solvent as it is a cheap, clean, and renewable resource [11–13].

To perform a wide spectrum of organic reactions in water, surfactants are vital owing to their ability to form micelles, which increase the solubility of organic compounds in water and allow organic reactions to take place in their core. Lipshutz has, for example, developed new surfactants: PTS (PEG-α-tocopheryl sebacate) [14], TPGS-750-M (PEG-α-tocopheryl succinate) [15], Nok (β-sisterol methoxypolyethyleneglycol succinate) [16], and PQS (PEG ubiquinol sebacate) [17], which allow Heck, [18–20] Suzuki–Miyaura [21–23], and Sonogashira [24] reactions to be carried out in the core of micelles dispersed in water. His group also developed a catalytic surfactant by grafting a Grubbs–Hoveyda catalyst to the polyethyleneglycol ubiquinol succinate (PQS) surfactant in order to perform cross-metathesis reactions in water [25]. However, the surfactant syntheses designed by Lipshutz do not fully adhere to the principles of green chemistry since they require the use of carcinogenic solvents such as toluene or dimethylformamide (DMF) as well as toxic stain-based catalysts [26]. Hence, the way for the development of green catalytic surfactants is still wide open.

Moreover, organocatalysis is preferred to metallic catalysis because organocatalysts are more resistant to moisture and oxidation while being generally cheaper and less toxic than metallic catalysts [27]. Developed by D. MacMillan, imidazolidinones constitute a class of organocatalysts which represents an alternative to Lewis acids as they act with the formation of an iminium ion, equivalent to a Lewis acid activation [28]. Imidazolidinones can be synthesized easily and they present a chiral amine which can lead to asymmetric synthesis [29]. This type of catalyst can perform a wide range of organic reactions such as Diels–Alder [30]. Friedel–Craft [31–33], aldolization [34,35], and Michael [36] reactions.

In this context and to comply with the principles of green chemistry, the strategy of the study centered on synthesizing a new bio-sourced surfactant, bearing an imidazolidinone moiety at the end of its hydrophobic part. Glycerol was chosen as the bio-sourced starting material for the hydrophilic part of the surfactant. In fact, this molecule is safe, renewable and abundant since it is a by-product of the formation of bio-diesel. With respect to the imidazolidinone moiety, phenylalaninamide, which is a derivative of phenylalanine, was selected for the purposes of the present study (Figure 1). The total synthesis of this target molecule was carried out in nine steps that were optimized, fully respect the principles of green chemistry [37]. The synthesized molecule was then characterized and its surfactant aspect evaluated.

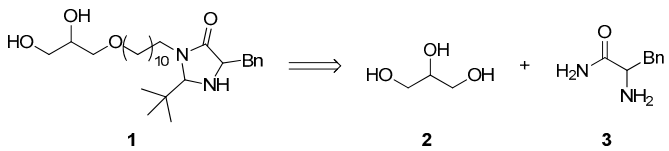

Figure 1. Retrosynthetic pathway of the targeted surfactant.

2. Materials and Methods

2.1. Physical Data and Spectroscopic Measurement

^{1}H NMR spectra were acquired with a FOURIER300 (300 MHz) spectrometer from Brüker Coporation (Karlsruhe, Germzany). The chemical shifts δ are expressed in parts per million (ppm) and referenced to tetramethylsilane at 0 ppm. Coupling constants J are expressed in Hertz (Hz). Data are reported as follows: δ, multiplicity (br: broad, s: singlet, d: doublet, dd: doublet of doublet, t: triplet, q, quadruplet, and m: multiplet), J, integration, assignment. All samples were diluted in deuterochloroform.

^{13}C NMR spectra were recorded on the same instrument at 75 MHz. Chemical shifts are referenced to the central peak of residual $CDCl_3$ (77.2 ppm).

Infrared (IR) spectra were recorded on a Spectrum 65 FT-IT spectrometer form Perkin-Elmer in ATR mode. Wavenumbers are expressed in cm^{-1}.

High Resolution Mass Spectra (HRMS) were obtained on a GCT Premier (Waters, Milford, MA, USA) mass spectrometer via direct introduction. Analyses were performed at the Institut Chimique de Toulouse, Université Paul Sabatier, 31062 Toulouse, France.

2.2. Chromatography

All reactions were monitored by thin-layer chromatography (TLC) on Merck pre-coated aluminum plates (silica gel 60 F254) and spots were revealed by dipping into Ceric Ammonium Molybdate (CAM) solution. The CAM solution was prepared with $Ce(SO_4)_2$ (5 g), $(NH_4)_6Mo_7O_{24}.4H_2O$ (25 g), and concentrated H_2SO_4 (50 mL) diluted with water (450 mL).

Flash chromatography was performed using silica gel 60 (particle size 0.040–0.063 mm) on 15, 35, 125, 300, 430, 720, or 1000 mL columns from Sodipro (Échirolles, France).

2.3. Usual Procedures

All reagents and solvents were obtained from commercial suppliers (Sigma Aldrich (St. Louis, MO, USA), VWR (Radnor, PA, USA), and CarloErba (Sabadell, Spain)) and used as received without further purification.

All air/moisture sensitive reactions were carried out in a nitrogen atmosphere using dry glassware and commercial anhydrous solvents.

All heated reactions were carried out using a Findenser condenser from Radley (London, UK), which requires no running water to operate. An oil bath was used to heat the reaction medium.

2.4. Tensiometry

Surface tension analyses were recorded on a 3S blade tensiometer from GBX (Lake Oswego, OR, USA). All analyses were performed at 23 °C. Each solution was measured three times until the surface tension was stabilized.

2.5. Dynamic Light Scaterring

DLS analysis was performed on a Zetasizer NanoZS from Malvern using semi-micro plastic dispensers of dimensions 12.5 × 12.5 × 45 mm from Brand. Each sample was run three times at 25 °C.

3. Results and Discussion

3.1. Synthesis of the Targeted Surfactant

The proposed pathway towards molecule **1** envisioned a convergent synthetic approach involving the coupling of **8** and **10** (Figure 2). The first steps of the synthesis of **8** were performed using recently published criteria [37]. Mesylated alcohol **6** was obtained in 39% overall yield following the optimized three-step linear sequence. Since the mesyl group is acid sensitive, compound **6** was not purified on silica gel, but was directly engaged in a deprotection reaction. Hence, the ketal moiety was removed in order to introduce stronger silyl ether protecting groups that could resist the drastic conditions expected for the rest of the synthesis.

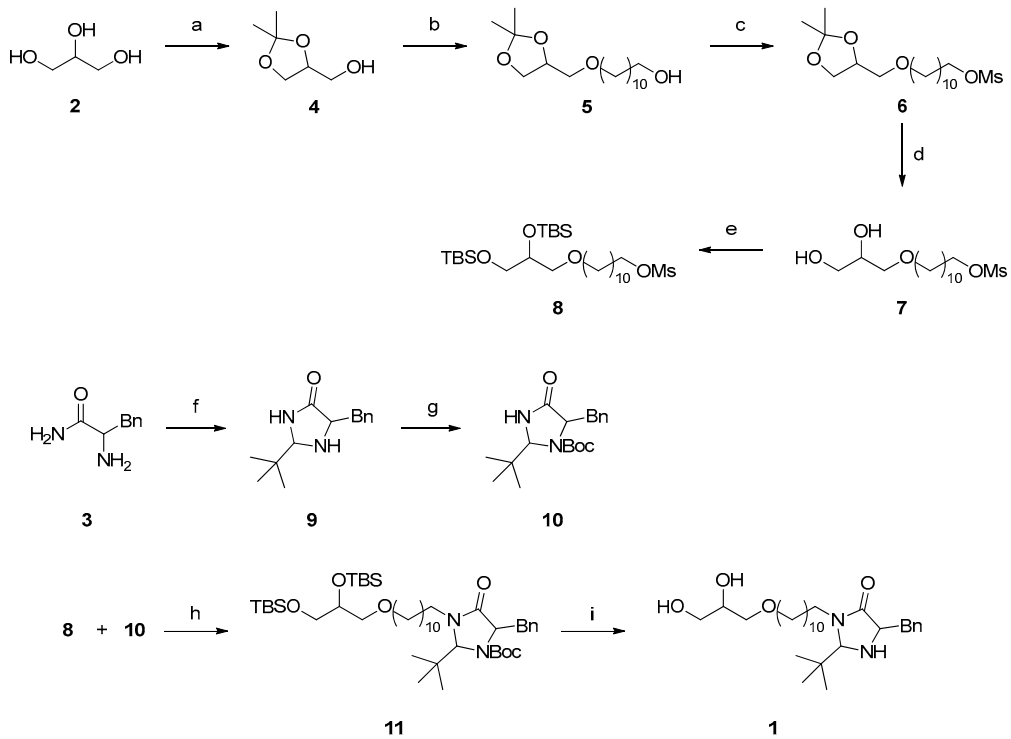

Figure 2. Total synthesis of the surfactant. (**a**) Montmorillonite K10 (20%w:w), acetone, RT, 3 h, 98%, (**b**) $Br(CH_2)_{11}OH$, NaOH, 4-MTHP, 80 °C, 5 h, 58%, (**c**) MsCl, TEA, MTHP, 0 °C, 3 h, 68%, (**d**) *p*TSA, MeOH, RT, overnight, 88%, (**e**) TBSCl, Imidazole, THF, RT, overnight, 88%, (**f**) pivaldehyde, $FeCl_3$, THF, 65 °C, 24 h, 86%, (**g**) Boc_2O, DCM, RT, overnight, 91%, (**h**) NaH (60% dispersed in oil), DMF, 60 °C, 8 h, 22%, (**i**) TFA, DCM, RT, overnight then TBAF, THF, RT, 5 h, 10%.

The acetonide **6** was thus deprotected using *p*TSA in methanol at room temperature [38]. The corresponding diol was isolated in good yield (88%) and then protected using *tert*-butyldimethylsilyl chloride and imidazole in anhydrous THF at room temperature to give the desired molecule **8** in 88% yield [39]. Molecules **7** and **8** (along with molecules **9**, **10**, **11**, and **1**) were characterized by HRMS, IR, ^{1}H and ^{13}C{^{1}H} NMR; original spectra are found in the Supplementary Materials.

The study then focused on the preparation of the imidazolidinone organocatalytic part using phenylalaninamide as a starting material. This compound is a derivative of phenylalanine, [40] which is an amino acid and can be considered as a bio-sourced starting material.

Phenylalaninamide **3** was then stirred with pivaldehyde using iron chloride ($FeCl_3$) as a catalyst in THF solvent at 65 °C to give 4-imidazolidinone **9** in 86% yield [41]. This reaction led to a 1:1 *syn*/*anti* mixture of diastereoisomers that could be separated on a silica gel column.

The amine moiety of the obtained 4-imidazolidinone **9** was then Boc-protected to deactivate this group prior to the coupling between **8** and **10**. This protection was performed with Boc_2O in DCM at room temperature [42]. Only the *syn* diastereoisomers reacted in these conditions leading to **10** in 91% yield. The *anti* diastereoisomers did not react even at higher temperatures.

The nucleophilic substitution between amide **10** and mesylated alcohol **8** was then realized in the presence of NaH (60% dispersed in mineral oil) in anhydrous DMF at 60 °C [43]. This reaction led to the desired tertiary amide **11** in 22% yield. Finally, the one-pot deprotection of the Boc and silyl ether groups of **11** was carried out by using trifluoroacetic acid (TFA) in dichloromethane (DCM) solvent at room temperature. Subsequent to the removal of the solvent, tetrabutylammonium fluoride (TBAF) and tetrahydrofuran (THF) were added [44]. After 5 h at room temperature, the targeted molecule **1** was successfully isolated in 10% yield. However, before envisaging any optimization of the final yields, the decision to evaluate the surfactant properties of the synthesized molecule was taken.

3.2. Effect on Surface Tension

Molecule **1**, obtained as a yellow oil, was dissolved in water. Its solubility saturation point was reached at 160 mg/L. The surface tension value of this solution, measured with a 3S Wilhelmy Blade tensiometer from GBX at room temperature, is 37.4 mN/m. Since this value is lower than that of pure water (72.2 mN/m), [45] compound **1** can thus be considered as a surfactant molecule.

Then, we progressively added this solution to pure water and measured the surface tension following each addition (Figure 3).

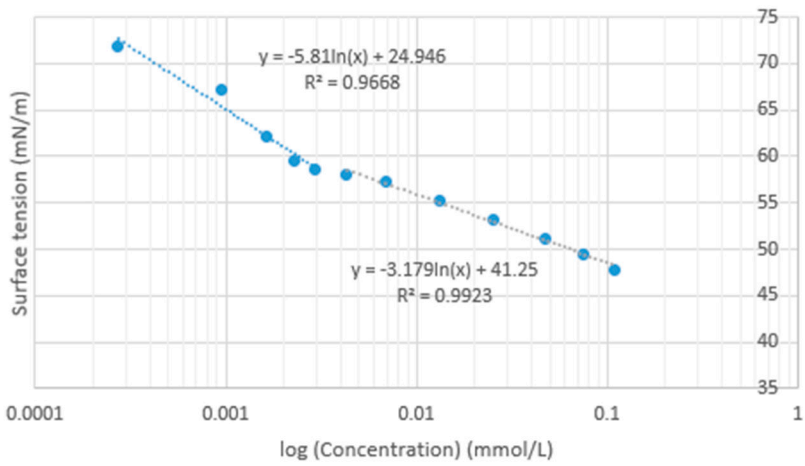

Figure 3. Evolution of the surface tension of a solution of surfactant in water.

As can be seen in Figure 3, the surface tension decreased when the surfactant was added. A change in slope was observed at 2.0×10^{-3} mmol/L, which indicates that the surfactant organization in the studied solution had changed. After this point, aggregates were formed, in a process called critical aggregation concentration (CAC). Nevertheless, we observed that the surface tension continued to decrease, indicating that at these surfactant concentrations, there could be a competitive process, between aggregate formation and surface adsorption.

3.3. Dynamic Light Scattering (DLS)

In order to determine the presence and the size of these aggregates, the solution with the greatest concentration was subjected to dynamic light scattering (DLS) analysis. The analyses were performed on a Zetasizer NanoZS from Malvern with semi-micro plastic dispensers with dimensions of 12.5 × 12.5 × 45 mm by Brand. Three runs were realized for the 160 mg/L solution at 25 °C as shown in Figure 4.

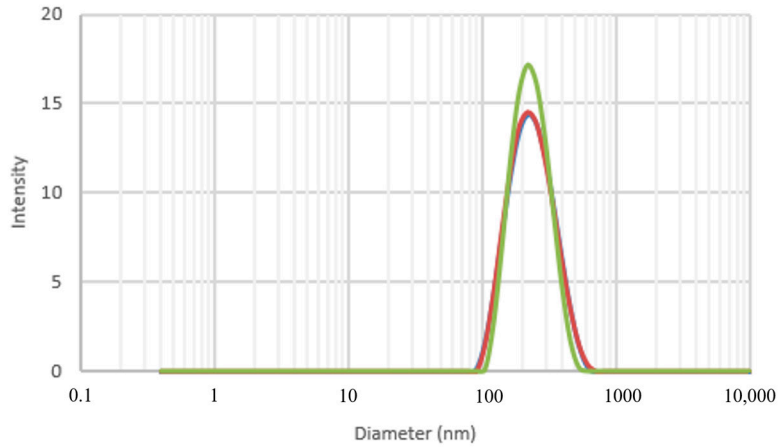

Figure 4. DLS analysis of the non-filtrated surfactant solution.

Only one population of aggregates was observed in this solution. The analysis was repeatable as the three runs were overlaid, with an average diameter of 217.8 ± 0.3 nm. This result correlated with the tensiometric measurements. Indeed, the size of our aggregates was too big for micelles, which vary approximately between 20 and 50 nm for Lipshutz's surfactants, for example [15].

The studied solution was then filtered on a 0.2 µm cellulose filter to reveal the possible presence of smaller aggregates. Results are shown in Figure 5.

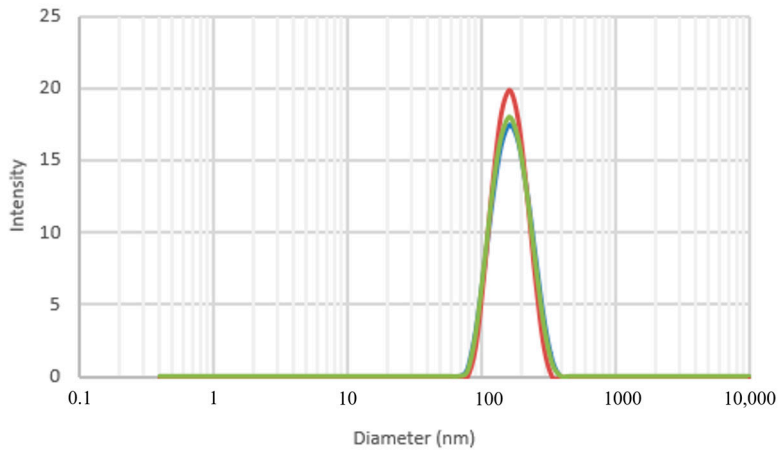

Figure 5. DLS analysis of the filtrated solution of surfactant.

As no small-sized particles were observed, we concluded that no micelles were formed. The average diameter was 158.0 ± 0.4 nm, which is highly likely due to the filtration which eliminated the biggest aggregates.

This size of aggregates is more typical of the formation of vesicles, [46] which are generally obtained with bolaform surfactants [47,48]. Compound **1** can be actually considered as bolaform as it has hydrophilic groups at both ends of the hydrophobic hydrocarbon chain. To form vesicles, the surfactant might fold owing to hydrogen bonds between the imidazolidinone and the glycerol moiety.

To check this hypothesis, density functional theory (DFT) modelling was performed.

3.4. DFT Modelling

The modelling was made using the Gaussian09 code in the framework of the Density Functional Theory (DFT) at the B3LYP/6-31+ G* level of theory [49,50]. The geometries of the surfactant and a glycerol ether (1-dodecylglycerol ether) were optimized in the gas phase and in water via the SMD method [51]. Calculations of the solvation energy of the two molecules were then carried out. The solvation energy of the synthesized surfactant was −23.28 kcal/mol while the solvation energy of the glycerol ether was −11.98 kcal/mol. and the imidazolidinone group is the only difference between the two molecules. Therefore, the logical conclusion is that this group rendered the surfactant more hydrophilic.

To confirm this hypothesis, the dipole moment was also calculated. The surfactant had a dipole moment of 8.2 Debye whereas the dipole moment of the glycerol ether was 5.1 Debye. Mulliken atomic charges were determined for the surfactant. The results showed the glycerol part had a charge of −0.13e. Those of the carbon chain and the imidazolidinone moiety were respectively −0.22e and +0.35e. The imidazolidinone and the glycerol parts thus exhibit opposed charges, the electrostatic interactions could lead to the formation of hydrogen bonds between those moieties. In fact, the hydrogen of the alcohol function had a charge of +0.54e and the nitrogen of the amine group had a charge of −0.41e, thus proving the formation of hydrogen bonds. The molecule thus folds to form the observed vesicles.

4. Conclusions

In conclusion, a new bio-based surfactant organocatalyst was synthesized. The surfactant scaffold was obtained from bio-based starting materials and bears an imidazolidinone moiety that should act as a chiral organocatalyst. The first steps of the synthesis were optimized using environmentally friendly conditions in order to fully respect the principles of green chemistry and resulted in a target surfactant with high purity. The amphiphilic character of the synthesized molecule was demonstrated with tensiometry studies. DLS and DFT modelling analyses indicate that the surfactant belongs to the bolaform category and that it is able to form vesicles in water, making it possible to envisage carrying out organic chemical reactions within these vesicles.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/suschem2020019/s1, HRMS, IR and NMR description of **7**, **8**, **9**, **10**, **11,** and **1**.

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