

## Synthesis and characterization of amphiphilic surfactants with hexadecyl (C<sub>16</sub>H<sub>33</sub>-) side chains for use in marine antifouling paints.

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### Abstract

In this work, two surfactants derived from cetyltrimethylammonium bromide (CTAB) were synthesized by telomerization reaction: N-hexadecyl, N-methyl, N-(1,1 dimethyl) ethoxy amin and zinc di-cetyltrimethylammonium. The first one is a surfactant with a linear hydrocarbon chain C<sub>16</sub>H<sub>33</sub>, the second one is a nanocomposite with two linear C<sub>16</sub>H<sub>33</sub> chains. The latter was prepared in distilled water as solvent and zinc dioxide at 50°C. The characterization of these two telomeres was obtained by nuclear magnetic resonance (<sup>1</sup>H NMR) and differential scanning calorimetry (DSC).

**Key words:** Surfactant; nanocomposite; antifouling; cetyltrimethylammonium bromide; differential Scanning Calorimeter.

### 1. Introduction

Ship hulls must be covered with an effective antifouling system to avoid the harmful consequences of biofouling, as this causes a serious problem for the shipping industry, such as vessel maintenance (corrosion) and fuel consumption (increased energy demand) [1-5].

The antifouling coatings that appeared in the 19th century [6] and managed to monopolize the coatings market are based on copper, arsenic, mercury oxide and organotin copolymers. However, they were largely banned in 2003 following the discovery of harmful effects on marine organisms [2,7-12].

These paints have been completely removed.

As a result, great efforts have been made to develop antifouling paints without tin and toxic compounds [10,11].

Some researchers have focused on coatings based primarily on the control of physicochemical and mechanical properties such as surface roughness and wettability, which impact the interactions between marine organisms and the treated surface [12,13]. Others have focused on

coatings based on new natural biocides, such as compounds from green algae [14-20].

Transition metal nanoparticle systems have very interesting physical properties and are used in various fields such as biological labeling [21, 23], medicine, sensors [24], light-emitting diodes (LEDs) [25], and environmental technology [26, 27]. ZnO<sub>2</sub> nanoparticles have promising applications in antifouling due to their high photoreactivity [28-32], low cost, chemical stability [33 -35] and non-toxic nature.

Supramolecular chemistry and nanostructured systems are the art of the century. The results indicate that ZnO<sub>2</sub> nanoparticles up to 1.0 wt % could make nanofillers with organic entities. This decreases water penetration between macromolecules [36-38] by forming a stronger, impermeable and more resistant gel. In the present work, we synthesized two surfactants, the first one enhanced by an acetone in the presence of ZnO<sub>2</sub> nanoparticles, the second surfactant with two chains linked by Zn.

The functional difference of these two products taken as a coating will be treated in another work. Our products are currently applied on plates fixed on a panel at a depth of 4 meters in the sea under well determined conditions (paragraphs 3.2 and 3.3).

## 2. Experience

### 2.1 Materials and measures

The N-hexadecyl, N-methyl, N-(1,1 dimethyl) ethoxy amin (product **1**) and the di-acetyl-trimethyl-ammonium of Zinc (product **2**), were synthesized in the laboratory of Sciences and Technology of Materials of the University of Djelfa -Algeria-, this synthesis is described in detail in the sections 2.2 and 2.3

Analytical products were used directly without further purification such as acetone, zinc dioxide ( $ZnO_2$ ) and distilled water ( $H_2O$ ). The solvents used for purifications were: acetonitrile, pentane, diethyl ether (Merck). Proton NMR measurements were performed on a Bruker WB 360 spectrometer (internal ref.  $CDCl_3$ ). Chemical shifts are expressed in  $10^{-6}$ .

Differential Scanning Calorimetry (DSC) allows to determine, as a function of temperature, the changes of state caused by physical (glass transition, melting, crystallization) or chemical (polymerization, oxidation, degradation) modifications of a material. Measurements were performed on a Mettler TA 4000 model apparatus at a heating rate of  $10^\circ C/min$ . The apparatus includes a mechanical gas compression cooling system to control the cooling of the furnace atmosphere. In this study, the most important interest is the glass transition temperature  $T_g$  and the melting temperature  $T_f$ .

The glass transition temperature ( $T_g$ ) was taken at the beginning of the jump corresponding to the heat capacity.

Several works have been performed by DSC to determine the phase diagrams of polymer blends and systems [39, 40], thermal properties (DSC) were performed in a temperature range of  $0^\circ C$  to  $1000^\circ C$ .

### 2.2. Preparation of N-hexadecyl, N-methyl, N-(1,1 dimethyl) ethoxy amin

Under a fume hood and to eliminate all toxic traces, 50 ml of acetone and 4 g of cetyltrimethylammonium bromide  $N(C_{19}H_{42})Br$  and a few milligrams of  $ZnO_2$  are introduced into a 100 ml two-necked flask equipped with a refrigerator and a thermometer. The temperature is set at  $50^\circ C$  with agitation for three hours.

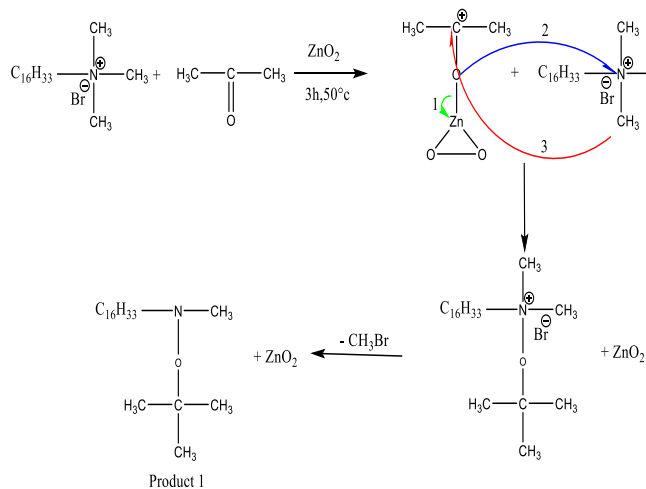
At the end of the reaction and after purification in acetonitrile, the solution is poured into a funnel fitted with filter paper. The liquid flows out by gravity while the paper retains the solid. The product obtained is dried under vacuum and put back in the oven at room temperature during one night. The methyl bromide gas is removed by the fume hood.

The yield of the reaction is 75%.

$\delta$  (ppm):  $^1H$  RMN (400 MHz,  $25^\circ C$ ,  $D_2O$ ):  $\delta = 3,34$  (m, 29H,  $-(CH_2)_n-N$ ; 2,39 (t, 2H,  $CH_2CH_2NCO$ ) ; 2,27 (s, 1H,  $(CH_3)_3CON$ ) ; 1,78 (s, 1H,  $(CH_3)N$ ).

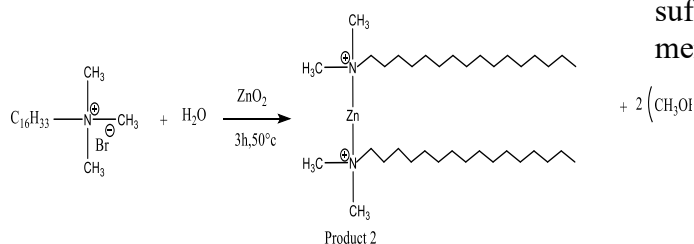
These surfactants are characterized by a hydrophilic aliphatic amine part. From an industrial point of view, they are manufactured from a fatty acid on which transformations are carried out to obtain an ammonium via an amide and a nitrile [41].

Many chemical reactions are required to obtain this family of surfactants; their manufacturing cost is significantly higher [42].



### 2.3 Preparation of Zinc di-cetyltrimethylammonium

In the same way as the previous reaction (paragraph 2.2) and in the fume hood, 20 ml of water as reagent, a few mg of  $ZnO_2$  and 2.92 g of cetyltrimethylammonium bromide  $N(C_{19}H_{42})Br$  are introduced at  $50^\circ C$  for three hours under stirring. Methyl hypobromite ( $CH_3OBr$ ) is removed by distillation as it is formed. The yield of the reaction is 82%.  
 $\delta$ (ppm): RMN  $^1H$  (400 MHz,  $D_2O$ )  $\delta = 3,91$  (s, 1H); 3,64 (m, (31) x2H); 1,92 (m, 2H).



## 3. Results and discussion

### 3.1 Thermal properties

The thermal properties of the oligomers: N-hexadecyl, N-methyl, N-(1,1 dimethyl) ethoxy amin (product 1) and di-cetyltrimethylammonium of Zinc (product 2) were evaluated under nitrogen at atmospheric pressure (see figure. 1). On the one hand, surfactant 1 (CTAB + Acetone +  $ZnO_2$ ) shows a very broad endothermic peak with a maximum at  $195^\circ C$ , which corresponds

to its melting temperature  $T_f$ . For this sample the  $T_g$  could not be detected (Figure. 1) probably because of the small change in its heat capacity during the glass transition. It is noted that the addition of  $ZnO_2$  plays a very important role for this phenomenon [43].

From these data, it is very interesting to mention that this resulting surfactant is thermo-plastic, its temperature  $T_f$  remains unchanged even after a second heating (See table.1). It is necessary to note the good correlation between these results and those given in the bibliography [44-46].

The second product (CTAB +  $H_2O$  +  $ZnO_2$ ) resembles that in figure. 2. It shows a sharp narrow exothermic peak at  $280^\circ C$  with a weight loss of 7.1%. There is some instability with a thermal shift around  $228^\circ C$ , which corresponds to the glass transition temperature  $T_g$ .

The exothermic peak on this sample (CTAB +  $H_2O$  +  $ZnO_2$ ) corresponds to the cold crystallization of the surfactant. The temperature of this peak varies only slightly with the addition of  $ZnO_2$  nanoparticles. In the literature Ray et al [43] worked on non-plasticized polymers and noticed a considerable decrease in  $T_c$  with the addition of nanoparticles (NP). They were thus able to conclude that a small quantity of NPs is sufficient to play a nucleating role on the polymer.

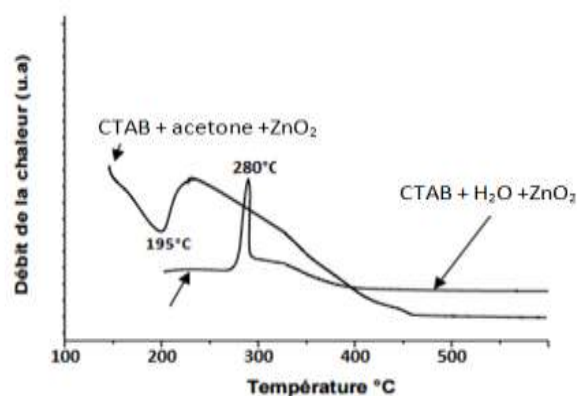


Figure. 1 DSC of both products 1 and 2

The CTAB emulsion (Figure. 2) shows two peaks even after a second heating, this is not

due to solvent evaporation. The first is around 260 °C and is due to crystallization, CTAB is a surfactant that has a melting point between 237-243 °C. Thermal decomposition starts after 400 °C and peaks at 435 °C. The transition temperature  $T_g$  is about 111 °C.

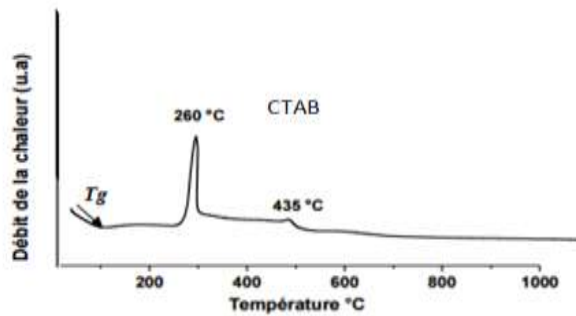


Figure. 2 DSC of CTAB Product

Products	$T_g$ (°C)	$T_c$ or $T_f$ (°C)
1	/	195
2	228	280
CTAB	111	260

Table.1: Characteristic temperatures of the surfactants.

### 3.2 Preparation of the paint and plates

The plates used are rectangular (7.5 cm x 6.5 cm) in Aluminum, thickness 3 mm (Figure.3). The test paints were applied directly using a flat brush on the surface of the plate previously scraped with sandpaper, cleaned and washed with methanol.

The paints are prepared by dissolving the resin (35 parts) in 2-methoxypropanol (65 parts). The formulations are prepared in a laboratory DI-SPERMAT dissolver.

Table. 2 shows all the paint formulations applied on these plates with different rates of biocides.

Biocide	Biocide content	Plate number
Without paint (control)	0%	I
TBT (plate II) [47]	10%	II
Surfactant. 1	10%	III
Surfactant. 2	10%	IV

Table.2 The different Products with their percentage.

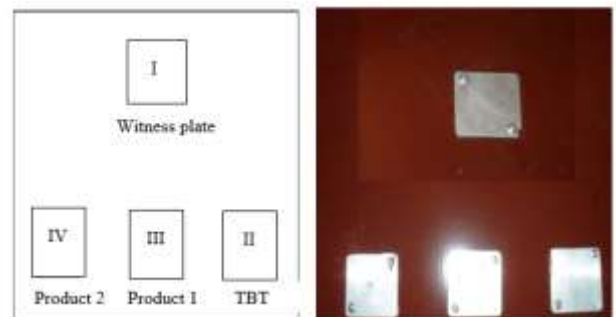


Figure.3 Metal support (February 1, 2022) before immersion.

### 3.3 Exposure to the marine environment

The painted plates were immersed at a depth of 4m in the port of Oran -the second economic city located in the west of Algeria- near the customs quay. They will remain twenty-four months (24 months) which corresponds to four cold and hot seasons.

These plates will be photographed and a study of their behavior with respect to the deposition of the underwater fouling will be carried out at a later date (February 2022 immersion date).

## 4. Impact on health

In Europe, nano products are introduced in several areas. Today, scientific research has not been able to control the lack of epidemiological data, to make a complete assessment of the potential risks associated with manufactured nanomaterials contained in all everyday consumer products.

However, an increasing number of publications concerning toxicological and eco-toxicological data for hazard assessment have been published. In 2013, the main nanomaterials used in these products worldwide are, in descending order, silver, titanium, carbon, silica, zinc and gold [48, 49]. They are found in many sunscreens as well as in some toothpastes. They are also present in the composition of clothing textiles because of their antibacterial properties. The number of products containing nanomaterials has doubled in five years [48-52]. Regulation 528/2012 specified that biocides containing nanomaterials must be subject to a specific authorization procedure and this from 1 September 2013 [53].

## 5. Conclusion

In recent decades, environmental protection concepts have led man to abandon coatings containing biocides that are toxic to non-target species (not responsible for marine biofouling). After the implementation of national and international regulations, limiting and then banning TBT-based paints, research has intensified in order to develop antifouling coatings that are both effective and environmentally friendly, but also adapted to the specificities of each use (size of vessels, duration and speed of travel, etc.). The development of biodegradable materials, nano-structured matrices, and the use of natural biocides obtained by extraction from the natural environment are promising.

In this study we have shown that it is possible to prepare stable, pure and non-toxic surfactants with one or two  $C_{16}H_{33}$ - chains in good yield. However, the introduction of Zn atom improves the solubility of these surfactants in organic solvents.

The glass transition temperatures are  $228^{\circ}C$  for product 2 and  $111^{\circ}C$  for the starting product (CTAB) almost half. For product 1 the  $T_g$  temperature could not be detected.

The decomposition temperatures are around  $400^{\circ}C$  which is quite suitable considering the presence of  $C_{16}H_{33}$ .

And in order not to significantly alter the basic properties of these surfactants, the amount of  $ZnO_2$  can be increased.

DSC also revealed that the crystallization and melting temperatures are incomparable but in good agreement with the results cited in bibliography.

There are no regulatory texts (national, European or international) concerning the risks of these substances for the environment and for humans (workers and users). The application of paint with these products will be discussed in other articles.

## 6. Perspective

Previous studies in our laboratory have led to the development of an original method for the synthesis of surfactants with amine and quaternary ammonium functions from very simple reagents.

These surfactants showed a bacteriostatic activity towards bacterial strains, even in the absence of ammonium functions (product 1). We have taken this know-how and modified it in order to adapt it to an application in the field of antifouling paints.

Our main perspectives of this work are, first, to elaborate coatings with amine (product 1) and quaternary ammonium (product 2) functions; then, secondly, to verify if they have inhibiting activities towards the marine organisms involved in the fouling phenomenon.

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