

Silica Nanocapsules Based on Gemini Surfactant As Environmentally Friendly Nanocontainers for Corrosion Protection in Seawater

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ABSTRACT

Encapsulation of active agents (corrosion inhibitors, pH indicators) has been described as a promising approach to impart controlled release and limit detrimental interactions between the active agents and the coating matrix. Mesoporous silica nanocapsules (SiNC) are engineered materials widely used for encapsulation. One synthesis route reported in the literature for these materials is based on a one-step emulsification process (oil-in-water microemulsion), using hexadecyltrimethylammonium bromide (CTAB) as emulsifier of the microemulsion. However, CTAB is also a source of toxicity to marine species, thus its replacement by other surfactants has been suggested.

This work describes the synthesis of new silica nanocapsules loaded with corrosion inhibitor 2-mercaptobenzothiazol (MBT) by using a gemini surfactant as a potential replacement for CTAB. The obtained nanocapsules were characterized by scanning electron microscopy (SEM), dynamic light scattering (DLS) and BET for pore size and surface area analysis. All the parameters were compared with those for nanocapsules based on CTAB, as well as ecotoxicity in relevant marine species. Nanocapsules were characterized by electrochemical techniques for anticorrosion applications, showing that they can be a prospective, new generation of nanomaterials with lower toxicity.

Key words: silica nanocapsules, gemini surfactants, encapsulation, corrosion protection, ecotoxicity

INTRODUCTION

One of the most common ways to protect metals from corrosion relies on the application of protective coatings. As a passive barrier, they prevent the contact between electrolytes and the metal structure. However, any mechanical damages, temperature or UV radiation may cause the coating's deterioration, which leads to loss of protection and consequently triggers corrosion processes.¹ Imparting active protection functionality in protective coatings via direct addition of corrosion inhibitors, is a common way to overcome this issue. However, when added directly to the coating, very often inhibitors not only act on the metallic substrate but also interact with the coating matrix. That undesired interaction results in inhibitor deactivation, fast coating degradation and constant leaching of inhibitor to the environment.² In this context, encapsulation of corrosion inhibitors in an inert nanomaterial, can ultimately avoid these problems. Nanocontainers with inhibitors can be dispersed in coating formulations and the active agent is released only when the coating is damaged.³

Mesoporous silica nanocapsules are a well-known and leading nanocontainer system due to their ease of preparation, having a high surface area and various applications.^{4,5} However, it has already been reported that the monomeric cationic surfactant hexadecyltrimethylammonium bromide (CTAB) used in silica nanocapsules synthesis, is a main source of nanocapsules toxicity and its substitution was consequently suggested.⁶ The replacement of CTAB with dimeric surfactants, known as gemini surfactants, may be a solution to overcome this issue. The current state of the art reports that gemini surfactants exhibit lower toxicity to fresh water species than their conventional analogues, including CTAB.⁷

2-mercaptobenzothiazole (MBT) is a well-known corrosion inhibitor.⁸ It has been found toxic to aquatic organisms (ECHA*) and despite that, it is still commonly used. It has already been stated that encapsulation of the active molecules may reduce their toxicity due to controlled release.⁶

The research presented herein focuses on the synthesis of novel, environmentally-friendly silica nanocapsules loaded with a corrosion inhibitor (MBT). The synthesis has been modified by using a less toxic gemini surfactant as a replacement for CTAB. Moreover, characterization of the capsules, ecotoxicity studies and their application for corrosion protection were also part of this work.

EXPERIMENTAL PROCEDURE

Materials

Ammonia solution (NH₄OH) (25%) was purchased from Merck. Hexadecyltrimethylammonium bromide (CTAB) (≥98%), tetraethyl orthosilicate (TEOS) (≥99%), diethyl ether, sodium chloride (NaCl) and 2-mercaptobenzothiazole (MBT) (≥97%) were purchased from Sigma-Aldrich. Ethanol (absolute) was purchased from VWR Chemicals and buffer solutions (pH 4 and pH 10) from Carlo Erba Reagents.

1,4-bis-[N-(1-dodecyl)-N,N-dimethylammoniummethyl]benzene bromide (QSB2-12) was synthesized as described in the literature.⁹

Synthesis of loaded silica nanocapsules (Si_QSB_MBT)

Si_QSB_MBT were prepared by modification of a method described in the literature.¹⁰ Conventional cationic surfactant CTAB used as a template surfactant was replaced with a less toxic gemini surfactant (QSB2-12). Silica nanocapsules were synthesized in a one-step process through an oil-in-water microemulsion (Figure 1). Diethyl ether was used as a co-solvent, ammonia as a catalyst and TEOS as a silica precursor. The water phase consisted of 0.2 g of QSB2-12 dissolved in 35 mL of water with 0.25 mL of ammonia solution being added afterwards. The oil phase was obtained by dissolving 0.05 g of MBT in 25 mL of diethyl ether. The latter was added (dropwise) to the water phase

* European Chemicals Agency, <https://echa.europa.eu/>

in order to obtain an oil-in-water microemulsion. Subsequently, 2 mL of TEOS was added dropwise to the microemulsion under controlled stirring (stirring bar: 20x6 mm) and kept in a closed vessel for 24h. The obtained product was filtered, washed with warm water (~ 40 °C) and dried at 60 °C.

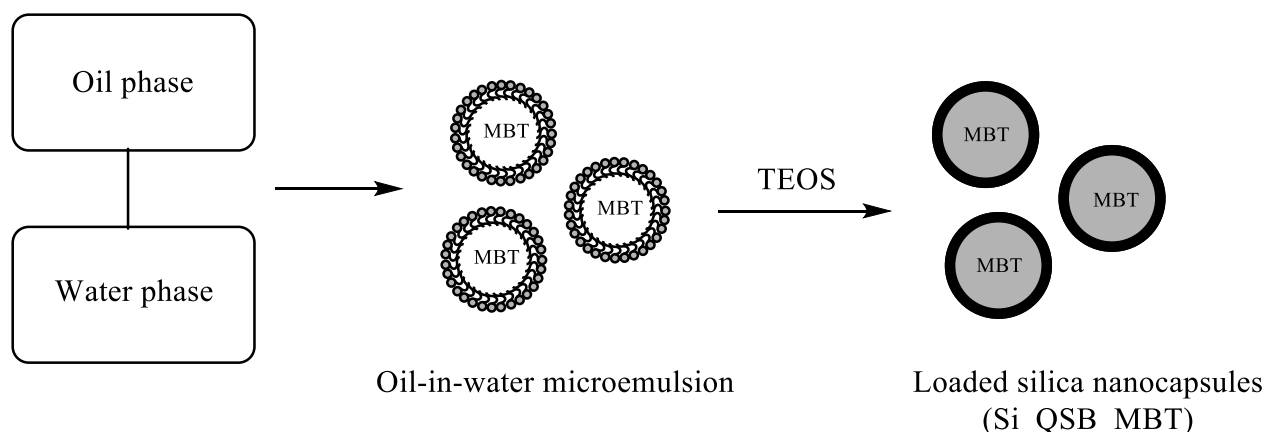


Figure 1: Synthesis of Si_QSB_MBT.

Characterization

Capsule morphology was characterized by scanning electron microscopy (SEM), analytical and high resolution Schottky emission (SE) (Hitachi SU-70[†] system with electron beam of 15 kV).

A Malvern Zetasizer Nano-ZS[‡] instrument was used to perform dynamic light scattering (DLS) and zeta potential measurements.

Textural properties of nanocapsules were evaluated based on the adsorption-desorption isotherms of N₂ at 196 °C, performed on the equipment Quantachrome NOVA 4200e[§]. Samples were previously degassed at 180 °C for 6h. The specific area (S_{BET}) was calculated by the BET method (Braunauer, Emmett and Teller), the total pore volume ($V_{\text{p}/p^0=0.98}$) was obtained from the volume of N₂ adsorbed at $p/p^0=0.98$. The most frequent pore diameters (ϕ_{pores}) was calculated by the BJH method (Barrett-Joyner-Halenda), applied to the desorption branch of the isotherm.²

Release studies of MBT from silica nanocapsules

The release profiles of MBT were determined by ultraviolet-visible spectroscopy (Scan Sci UV-VIS spectrophotometer^{**}).

In order to determine the total amount of MBT encapsulated, 20 mg of Si_QSB_MBT nanocapsules were dispersed in 20 mL of ethanol and kept under a stirring speed of 500 rpm for 24 and 48h. 2 mL of resulting solution was extracted with a syringe, filtered and analyzed by UV-VIS (wavelength 326 nm). Due to high absorbance values, supernatant was diluted four times. Four replicates were prepared. The encapsulation efficiency was calculated by Equation 1:

$$\%E = (n_{\text{MBT}_{\text{ext}}}/n_{\text{MBT}_{\text{in}}}) \times 100 \quad (1)$$

Where $n_{\text{MBT}_{\text{ext}}}$ is the total amount of MBT extracted from Si_QSB_MBT and $n_{\text{MBT}_{\text{in}}}$ is the initial amount of MBT used in the encapsulation.

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The release profiles were studied under different pH conditions (pH=4, 7 and 10). A mass of 20 mg of capsules was dispersed in an aqueous solution and left under stirring for 24h. 2 mL aliquots were removed at specific times within a period of 24h using a syringe with a filter (0.20 µm pore size) and analyzed by UV-VIS. The wavelength corresponding to the maximum of absorbance was found to vary with pH: 324 nm (pH=4), 321 nm (pH=7) and 309 nm (pH=10). For each pH three replicates were prepared. Dilutions were performed when needed. The correlation coefficients (R^2) of the calibration curves, from at least 5 standards, were higher than 0.998.

Ecotoxicity testing

Ecotoxicity of two surfactants, CTAB and QSB2-12, in artificial seawater (ASW) was studied. Cationic surfactants were tested on relevant marine microalgae (*Nannochloropsis gaditana*, *Phaeodactylum tricornutum*, *Tetraselmis chuii*) and crustacean species (*Artemia salina*), following standard protocols with some adaptations.⁶ For each compound, five concentrations plus one negative control (ASW only), with four (microalgae) and three (crustacean) replicates per treatment, were tested. For microalgae, each replicate contained 1 mL of contaminant (ASW for the control) and 1 mL of microalgae sample and tests lasted 72h, whereas for crustacean each replicate contained 1 mL of contaminant (ASW for the control) and ten animals, and tests lasted up to 48h. Preliminary tests were run for concentrations with logarithmic growth: 0.01-100 mg/L. Definitive exposure tests included a concentration range dependent on the tested species and chemical.

In order to classify the toxicity of the tested chemicals, obtained results (median lethal (LC_{50}) and median effect (EC_{50}) concentrations) were categorized according to the EC Directive 93/67/EEC scheme.¹¹

Anticorrosion efficiency of MBT in solution and Si_QSB_MBT

2024-T3 aluminium alloy provided by Service Centres Aero France^{††} with the following composition was used: Cr max. 0.1%; Cu 3.8-4.9%; Fe max. 0.5%; Mg 1.2-1.8%; Mn 0.3-0.9%; Si max. 0.5%; Ti max. 0.15%; Zn max. 0.25% and Al balance.

Alloy samples were polished with abrasive papers with different grit sizes, washed with distilled water and dried with compressed air. No additional pre-treatment was performed.

The corrosion measurements were carried out using a conventional three-electrode cell (placed in a Faraday cage) with a platinum counter electrode and a saturated calomel electrode (SCE) as a reference electrode and the aluminum alloy 2024 (1 × 1 cm² embedded in epoxy mold) as a working electrode. Electrochemical impedance spectroscopy (EIS) measurements were carried out using a Gamry FAS2 Femtostat with a PCI4 Controller^{‡‡}. Impedance spectra were obtained over a frequency range of 1 × 10⁵ Hz to 1 × 10⁻² Hz with a 10 mV sine wave as the excitation signal at open circuit potential, taking 7 points per decade. All measurements were carried out at room temperature.

The electrolyte was 50 mM NaCl. The measurements were carried out after 24h of immersion in 50mM NaCl (blank), 0.1 mM of MBT (MBT in solution), 0.1 mM of encapsulated MBT in Si_QSB_MBT (corresponding to 40 mg) and empty Si_QSB (40 mg).

RESULTS

Characterization of Si_QSB_MBT

Silica nanocapsules loaded with MBT were obtained as powder. Synthesis of Si_QSB_MBT is a result of a dynamic cross-coupling of two processes: dynamic gasification of the template and stabilization process of TEOS condensation together with self-assembly controlled by the presence of cationic surfactant. Polymerization of TEOS is an exothermic process causing gasification of the volatile co-solvent (diethyl ether) from the center to outside of nanocapsules.²

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