



Pure short-chain glycerol fatty acid esters and glycerylic cyclocarbonic fatty acid esters as surface active and antimicrobial coagels protecting surfaces by promoting superhydrophilicity

Romain Valentin^a, Marion Alignan^a, Géraldine Giacinti^a, François N.R. Renaud^c, Bernard Raymond^b, Zéphirin Mouloungui^{a,*}

^a ENSIACET – Unité Chimie Agro-Industrielle – UMR 1010 INRA/INP-ENSIACET 4 Allée Emile Monso 31030 Toulouse Cedex 4, France

^b BR Consultant 250, rue de Catox 40440 Ondres, France

^c UMR-CNRS-5510 Matis/I2B, Interactions Biologiques et Biomatériaux, Nosoco.tech®, Université Lyon 1, 8 avenue Rockefeller, 69373 Lyon Cedex 08, France

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ABSTRACT

Pure glycerol fatty acid esters and glycerylic cyclocarbonic fatty acid esters have an amphiphilic structure, giving these biomolecules a broad range of physico-chemical and biological properties. Physico-chemical properties depend on chain lengths, odd or even carbon numbers on the chain, and glyceryl or cyclocarbonic polar heads. The spectrum of melting-point values for these molecules is large. Surface-activity is very important and through determination of the critical aggregation concentration (CAC), some fatty-acid esters are considered as solvo-surfactant biomolecules. Coupling these self-aggregation and crystallization properties, superhydrophilic surfaces were obtained. An efficient durable water repellent coating of various metallic and polymeric surfaces was allowed. Moreover, these fatty acid esters promoting superhydrophilicity showed biological activity against Gram positive, Gram negative, and yeast-like micro-organisms. Such surfaces coated by self-assembled fatty acid esters in a stable coagel state present a novel solution to surface-contamination risks from pathogen proliferation.

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1. Introduction

Coatings designed to exhibit extreme wetting characteristics such as superhydrophobicity and superhydrophilicity have the potential to open up entirely new avenues for manipulating and controlling the interaction of liquids with surfaces [1]. Self-cleaning, antifogging, and bacteria-resistant surfaces are but a few examples of some of the applications that could be enabled by the creation of surfaces that either completely resist wetting by water (superhydrophobic state) or that are completely and instantaneously wet by water (high hydrophilic and superhydrophilic states). Superhydrophilicity and superwetting surfaces refer to textured and/or structured materials (rough and/or porous) on which water (liquid) spreads completely [2]. To obtain such surfaces, two basic approaches have been reported [1]. The first involves the use of photochemically active materials such as TiO₂ that become superhydrophilic after exposure to UV, or with suitable chemical modifications, visible radiation. Surface coatings based on TiO₂ typically lose their superhydrophilic qualities within minutes to hours when placed in a dark environment, although much progress

has been made toward eliminating this potential limitation. The second case involves the use of textured surfaces to promote superwetting behavior.

In nature, superhydrophilicity has been developed by different organs of plants and is caused by different micro- and nanostructures [3]. Superhydrophilic plant surfaces can be divided into those that are permanently wet, absorb water over their surfaces and let water spread over the surface. In the last case, water droplets spread rapidly on the peristome and form thin films, which make the peristome extremely slippery for insects [4]. Fast water spreading was observed on the leaves plants where glands secrete hydrophilic substances like saponins that, in combination with the surface roughness, lead to the superhydrophilicity. Water spreading is favored when surface roughness presents an arrangement where capillarity phenomena occur [3]. The superhydrophilicity provides a faster evaporation of the water by an increase of the water–air interface. Thus, water evaporates from a superhydrophilic surface much faster than that from a hydrophilic or superhydrophobic one, where water forms semi-spherical or spherical droplets. Indeed, saponins have detergent properties, which reduce the surface tension of the water and are known for their antimicrobial and antifungal properties [5]. Based on these observations, saponins cause the efficient spreading of water, and spreading of

* Corresponding author. Fax: +33 534323598.

E-mail address: zephirin.mouloungui@ensiacet.fr (Z. Mouloungui).

the water–saponin solution functions as an efficient mechanism of self-protection against biofilm formation.

In this work, we studied surface-active molecules such as fatty acid esters to respond adequately to the question of water-retaining by polymorphic liquid crystalline phases combining order and mobility at a molecular and supramolecular level. Therefore, glycerol fatty acid esters “monoglycerides” and “glycerol carbonate esters” are of great importance. These surfactants show self-assembly phenomena if their concentration is higher than a certain critical aggregation concentration (CAC). Face to the risk of pathogen contamination on the surfaces as cooling circuits [6] in manufactures, chlorine or metal based treatments are used which are damaging to the environment. Although these treatments have an antimicrobial action on free pathogens, they have no action on the fixation of biofilms which constitute a dynamic reservoir of pathogens that can reinfest circuits. An effective solution to this problem would be to make the wall surfaces anti-adhesive and antimicrobial [7–10] by adsorption of non-ionic fatty acid esters on metallic and polymeric surfaces [11,12].

We studied in this work the coating of surfaces by various highly purified glycerol fatty acid esters and cyclic carbonic fatty acid esters [13,14]. Pure GM-Cs present a free glycerol polar head. ‘Self-assembly’ refers to the autonomous organization of components into patterns or structures without human intervention [15]. At the nanometer-scale this process is governed by a delicate balance of different non-covalent forces exhibited between the molecules, such as electrostatic, van der Waals or hydrogen bonding [16]. There are some examples of self-assembly structures formed by polar lipids including glycerol fatty acid esters [15]. Carbonic glyceric fatty esters or GCE-Cs present a locked polar head glycerol. Pure GM-Cs are associated with variable lengths of hydrophobic chains (7–18 atoms of carbon), giving them an amphiphilic character and polymorphic properties. Evaluation of their antimicrobial properties was combined with their physico-chemical properties such as solvo-surfactivity and their ability to give to surfaces a textured morphology giving them a superhydrophilic character.

2. Methods

2.1. Materials and chemicals

Undecylenic and heptanoic fatty acids were obtained from Arkema (Colombes, France). Other fatty acids, glycidol (2,3-epoxypropan-1-ol, 96%), octanoyl, heptanoyl, lauroyl, and stearoyl chlorides, potassium hydrogen carbonate, molecular sieve 3 Å, glycerol, and anhydrous magnesium sulfate (95%) were supplied by Aldrich (L’Isle d’Abeau Chesnes, France). Glycidol was used after thin film distillation. Dodecylbenzenesulfonic acid (DBSA) was supplied by Acros Organics (Morris Plains, USA). The anionic resin, Ambersep A900-OH⁻, was purchased from Rohm & Haas (Lauterbourg, France). Industrial surfaces of copper (Cu), steel (St), and stainless steel (SSSt) were purchased from Descour&Caubaud (Lyon, France) and polyvinyl chloride (PVC) was from Nicoll (Cholet, France). They were cut in pieces with dimensions of 10 cm × 5 cm × 5 mm. These were carefully cleaned with water and then with acetone before being dried and stored away from dust. We note that these surfaces were not subjected to specific treatment, the roughness was not controlled, and the storage was in an uncontrolled atmosphere (no temperature, humidity, and oxidation control). The pure 99% glycerol carbonate was supplied by the company Huntsman (St. Mihiel, France) or obtained by flash distillation of crude glycerol carbonate in our laboratory [17–19]. Pure triethylamine was purchased from the company Sodipro (Echirolles, France), dichloromethane and soda from Gaches Chimie (Toulouse, France).

Synthesis of GM-Cs by esterification reaction of the fatty acids with glycerol was performed according to the methods of Eychenne and Mouloungui [20]. The other method used to obtain GM-Cs through condensation of fatty acids with glycerol was developed by the same team [21–24]. Glyceric cyclocarbonic fatty acid esters (GCE-Cs) were synthesized by acylation of glycerol carbonate with acyl chloride following the method described by Mouloungui and Pelet [14].

Escherichia coli (CIP 54127), *Staphylococcus aureus* (CIP 4.83), *Pseudomonas aeruginosa* (ATCC 15442), and *Candida albicans* (ATCC 15442) were purchased in international collections and *Enterococcus faecalis* (nosoco 20.7) was a clinical strain belonging to Nosocotech® collection.

Mueller–Hinton agar (Scharlau, Spain), tryptic soy broth (Difco, France,) and peptone/salt diluent (Difco, France) were commercially purchased.

2.2. Chemical analysis

GM-Cs and GCE-Cs were analyzed by gas chromatography using a Perkin Elmer Autosystem XL equipped with a 15 m × 0.25 mm i.d CPSIL8CBMS capillary column operating at 1.0 mL min⁻¹ He flow, an injector at 250 °C, a flame ionization detector FID at 340 °C, and an oven temperature ramp: 40 °C, for 0.5 min, ramp 40–90 °C at 50 °C min⁻¹, hold 2, ramp 90–250 °C at 20 °C min⁻¹. Structures of GM-Cs and GCE-Cs were confirmed by Fourier transformed infra-red (FTIR) spectra on KBr pellets using a Jasco FT/IR 460 Plus and ¹H NMR spectra recorded in CDCl₃ using a Bruker Avance 500 (500.13 MHz ¹H).

2.3. Physico-chemical characterization

A 3S tensiometer (GBX, France) was used to measure the surface tension of solutions by Wilhelmy plate technique to determine the critical micellar concentration (CMC) and critical aggregation concentration (CAC) of GM-Cs and GCE-Cs in aqueous solution. Wettability of surfaces was determined by the sessile drop technique, employing a Digidrop goniometer (Contact Angle Meter—GBX Scientific Instruments, France), coupled with the WinDrop⁺⁺ software to capture and analyze images. The results given are the average of at least five water contact angle measurements per sample. Using contact angle we can use the Young’s equation [25]:

$$W_{LS} = \gamma_{LV}(1 + \cos \theta) \quad (1)$$

where W_{LS} is the surface energy, γ_{LV} the surface tension and θ the contact angle between the liquid drop and the flat surface. Melting points are measured with a power modulation DSC device Pyris 1 (Perkin Elmer, USA), equipped with an Intracooler cooling system. The purge gas is nitrogen at a flow rate of 20 mL min⁻¹. Indium ($T_f = 156.6$ °C) and distilled water ($T_f = 0$ °C) are used for temperature calibration. Data were analyzed using the Pyris software (Perkin Elmer). Hermetic O-ring stainless steel capsules are used. An optical microscopy apparatus Nikon Eclipse E600 (Nikon Corporation, Japan) with crossed polarized filters is used to determine the self-organization of the fatty-acid esters studied. Images were acquired by a high resolution, low-noise CCD Nikon DXM-1200 color camera and analyzed using the LUCIA G (Laboratory Universal Computer Image Analysis) ver. 4.8 software. The surface morphology was analyzed by scanning electron microscopy (SEM) using a JEOL electron microscope (JSM-6400F) at 12 kV. Samples were coated with silver under vacuum by a SPI sputter unit.

2.4. Evaluation of the minimum inhibitory concentration (MIC)

According to Mayaud et al. [26] bacterial strains were cultured overnight at 37 °C and suspended in Mueller–Hinton broth to

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