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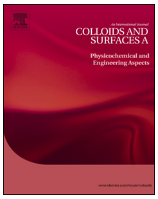

Interfacial activities and aggregation behaviors of *N*-acyl amino acid surfactants derived from vegetable oils

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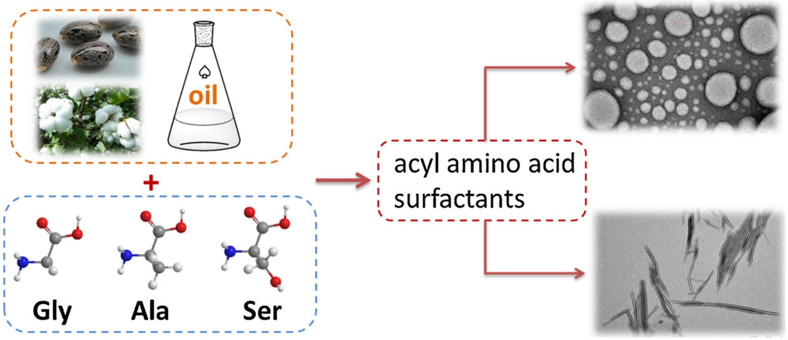
GRAPHICAL ABSTRACT



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ABSTRACT

The development of amino acid surfactants which are considered to be biodegradable and less toxic than traditional surfactants has been a subject of growing interests among chemists for the past 20 years. Within this category, *N*-acyl amino acid surfactants are popular due to their excellent interfacial properties and antimicrobial activities. In the present work, six new *N*-acyl amino acid surfactants were synthesized using vegetable oils (castor oil and cottonseed oil) and amino acids (glycine, alanine, and serine). Surface active properties of these surfactants were investigated. With the amide bonds acting as hydrogen bond donors and acceptors, globular and tubular vesicles were observed in the aqueous solutions of some prepared surfactants. The results indicated that hydroxyl groups on the hydrophobic tails for castor oil derivatives were associated with spherical vesicles formation, whereas serine residues bearing hydroxyl groups may be associated with the tubular vesicles.

1. Introduction

Over the past few decades, the rising environmental awareness of both governments and consumers has had a strong impact on the choice of surfactants. Therefore, environmentally benign surfactants based on natural building blocks, as a potential substitute for traditional petroleum-based surfactants, have received growing attentions [1]. Amino acids with carboxyl and amino groups are recently employed for the preparation of surfactants due to their excellent biodegradability and versatile properties [2,3]. Amino acid based surfactants usually have desirable properties, such as, low toxicity, non-irritation, low allergenic potential, good biodegradability, and harmless to marine

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organisms [4–6].

In particular, anionic *N*-acyl amino acid surfactants have been widely used in various areas [7,8], e.g., personal care products, cosmetics, household products, and detergents because of their good physicochemical properties and antimicrobial activities [9]. These surfactants have been reported to self-assemble into aggregates of various shapes induced by both hydrophobic effects and hydrogen bondings with the amide bonds acting as both donors and acceptors [2,10,11]. Therefore, the studies of the physical properties of *N*-acyl amino acid surfactants have both practical and theoretical significance.

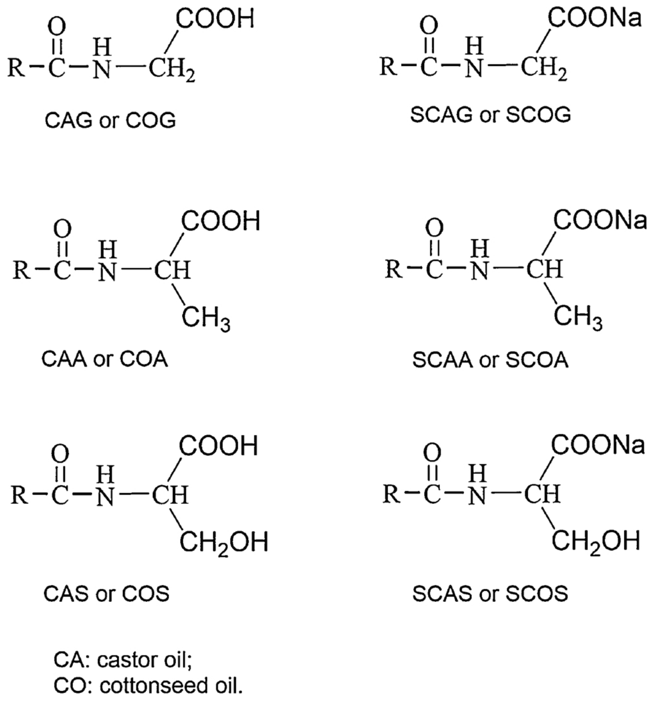
Traditionally, *N*-acyl amino acid surfactants are commercially produced by Schotten-Baumann reaction with fatty acyl chloride and amino acid reacting at high temperature [12]. However, the fatty acyl chlorides employed in this process are toxic; undesirable by-products and odor can't be eliminated. Previously, our group has reported green synthesis of acyl glycine surfactants using oils (coconut, peanut and soybean oils) and sodium glycinate [13]. In the present work, we have synthesized six new *N*-acyl amino acid surfactants derived from castor and cottonseed oil with glycine, alanine, and serine residues as headgroups. Castor oil is a well-known source of ricinoleic acid bearing a hydroxyl group on the 12th carbon, and has been used as additives in food, medicine [14,15], surface coating [16], and lubricants [17]. On the other hand, cottonseed oil, commonly used as frying oil, consists lots of unsaturated fatty acids without hydroxyl groups. We study and compare the interfacial activities and assembly behaviors of surfactants synthesized from these two vegetable oils in hope of shedding light on the role of hydroxyl groups. Remarkably, vesicle formation was associated with the presence of hydroxyl groups on surfactant structures, and the morphologies of vesicles depended on the hydroxyl group position.

2. Materials and methods

2.1. Materials

Cottonseed oil and castor oil were analytical grade and purchased from Acros Organics. All amino acids, glycine (99%, Macklin), alanine (99%, Macklin), serine (99%, Macklin) were used as received. Other reagents were also used as received. All solutions were prepared with deionized water ($\rho = 18.25$ MΩ•cm).

The acyl amino acids derived from vegetable oils, i.e., acyl glycine derived from castor oil (CAG), acyl glycine derived from cottonseed oil (COG), acyl alanine derived from castor oil (CAA), acyl alanine derived from cottonseed oil (COA), acyl serine derived from castor oil (CAS), and acyl serine derived from cottonseed oil (COS), were synthesized by a green method reported by our group [13]. Scheme 1 summarized the synthetic route of these surfactants. Amino acids were neutralized by NaOH aqueous solutions in three-necked flasks. The water was then evaporated, followed by the addition of corresponding vegetable oils and catalytic amount of CH_3ONa while stirring. The reaction mixtures were stirred at 160 °C for 5 h. After cooling, the mixtures were dissolved in water. White or yellow precipitates were formed upon the acidification by HCl aqueous solutions (Scheme 2).



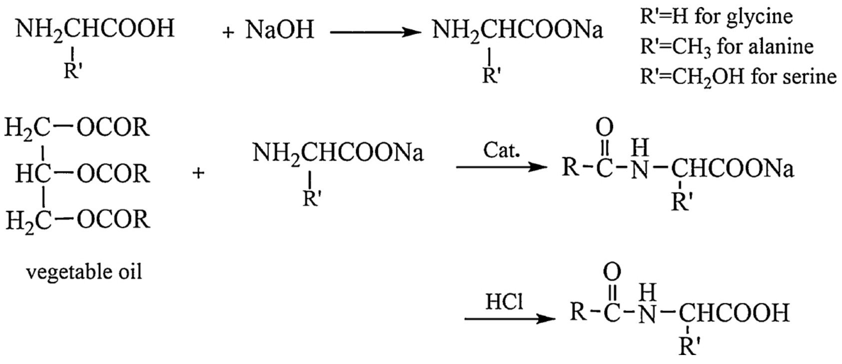
Scheme 2. Chemical structures of synthesized acyl amino acid surfactants (acidic forms and anionic forms).

The acyl amino acid surfactants, i.e., the corresponding sodium salts of CAG, COG, CAA, COA, CAS, and COS, were prepared by neutralizing the acyl amino acids with NaOH aqueous solutions to pH 8–9 until completely clear solutions were obtained. These sodium salts were named as SCAG, SCOG, SCAA, SCOA, SCAS, and SCOS, respectively.

2.2. Structure characterization

The composition of cottonseed oil and castor oil were characterized by GC–MS on an Agilent Technologies 700GC/MS-7890 A GC system using a methylation method [18]. The chemical structures of the six acyl amino acids were analyzed by both infrared (IR) spectra on a Thermo Fisher Nicolet iS10 FTIR spectrometer and mass spectroscopy (MS) using an AB SCIEX API3200LC/MS/MS spectrometer.

CAG: yield 90%. IR (v_{max}, cm^{-1}): 3316 (N–H), 1645 (amide band I), 1549 (amide band II). ESI-MS: m/z = 312.1, 336.0, 338.0, 340.1, and 353.9 are assigned to palmitoyl glycine (C16:0), linoleoyl glycine (C18:2), oleoyl glycine (C18:1), stearoyl glycine (C18:0), and ricinoleoyl glycine (C18:1,containing −OH), respectively.



Scheme 1. Synthesis of acyl amino acids from vegetable oil and sodium salts of the corresponding amino acids.