Effect of variations in the fatty acid chain on functional properties of oligofructose fatty acid esters

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A B S T R A C T

Oligofructose fatty acid esters are surfactants that considerably lower the surface tension of an air/water interface, provide the interface with a high dilatational modulus and lead to a high foam stability. In this study, we investigate the effect of the molecular structure of oligofructose fatty acid esters on their functional properties. We varied the length and degree of saturation of the fatty acid chain, and the number of fatty acids esterified to the oligofructose part. A tensiometer was used to establish CAC curves, light scattering to determine the size of micellar aggregates and an ellipsometer to determine the amount of material that adsorbed at the interface. Esters with a more hydrophobic character had a lower CAC and had a higher efficiency. Oligofructose mono- and di-esters with fatty acid chain lengths between C8 and C16 formed spherical micelles, while esters with a fatty acid chain length of C18 formed larger aggregates. The effectiveness was similar for all esters. Using the Gibbs adsorption model, we did not find major differences in the area per molecule for the different esters. Ellipsometry experiments also did not indicate major differences in the area per molecule for the oligofructose mono-esters. The area per molecule of oligofructose esters was larger than that of sucrose esters and independent of the degree of saturation of the fatty acid chain. We conclude that the amount of interfacial area occupied by one molecule is determined by the oligofructose part.

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1. Introduction

Two major types of food-grade surfactants are proteins and low molecular weight (LMW) surfactants (Bezelgues, Serieye, Crosset-Perrotin, & Leser, 2008; Rodríguez Patino, Carrera Sánchez, & Rodríguez Niño, 2008). Proteins are macromolecules with both hydrophilic and hydrophobic patches. Upon adsorption to the interface, they lower the surface tension and can unfold to create a network with high viscoelasticity (Bezelgues et al., 2008; Bos & Van Vliet, 2001). This network provides the interface with a high dilatational modulus. In contrast, LMW surfactants are relatively small and have a clearly defined hydrophobic and hydrophilic part. Upon adsorption to the interface, LMW surfactants can lower the surface tension much more than proteins. This is caused by a more compact interfacial structure of the LMW surfactants (Bos & Van Vliet, 2001). However, they do not typically create interfaces with a high dilatational modulus (Bos & Van Vliet, 2001; Kotsmar et al., 2008;

Wilde, Mackie, Husband, Gunning, & Morris, 2004). Instead, LMW surfactants stabilize interfaces by the Gibbs–Marangoni mechanism. This mechanism relies on rapid surface diffusion of surfactants that will reduce surface concentration gradients that can develop after deformation of the interface (Schramm, Stasiuk, & Marangoni, 2003; Wilde et al., 2004). Both surface tension and surface rheological properties are important with respect to foaming properties. A molecule that lowers the surface tension considerably and at the same time provides a high dilatational modulus could be an excellent foam stabilizer.

Previous research on oligofructose fatty acid esters showed that they have this ability to lower the surface tension of an air/water interface considerably, like an LMW surfactant, and to provide a high dilatational modulus, like a protein (Sagis, Boeriu, Frissen, Schols, & Wierenga, 2008; Van Kempen, Boeriu, et al., 2013; Van Kempen, Maas, Schols, Van der Linden, & Sagis, 2013). Both factors are important in surfactant performance and resulted in high foam stability. The oligofructose that was used was a mixture of oligomers with a degree of polymerization varying between 2 and 8 (average 4.4). Consequently, the resulting esters are also mixtures. By varying the size and number of hydrophobic groups, products

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with a wide range of amphiphilicity can be produced. This will have an impact on the functional properties of the molecule (Bos & Van Vliet, 2001).

The goal of this study was to determine the influence of variations in chemical fine structure on the functional properties of oligofructose fatty acid esters. To obtain a range of molecules with different functionality, the length of the saturated fatty acid chain (C8, C12, C16, C18) as well as the number of fatty acids per oligofructose molecule was varied (mono-esters for all four fatty acid chain lengths and also di-esters for C8 and C12). To investigate the influence of the degree of saturation on the functional properties, we also studied an ester of oligofructose and palmitoleic acid, a mono-unsaturated fatty acid with a chain length of 16. Additionally, to study the influence of the size of the hydrophilic group, sucrose esters were included. We have determined the surface tension of air/water interfaces stabilized by the different esters as a function of the bulk concentration to establish the CAC. From the CAC curves, we have derived the efficiency, effectiveness, the maximum surface excess concentration and the cross-sectional area per molecule. We have performed light scattering experiments to determine the size of the aggregates that were present above the CAC. Finally, we have studied the amount of material that adsorbed to the interface using ellipsometry.

2. Materials and methods

2.1. Materials

Oligofructose fatty acid esters were prepared according to a previously described protocol (Van Kempen, Boeriu, et al., 2013), by esterification of fatty acids with oligofructose with a DP ranging from 2 to 8, using lipase as a catalyst. Five different fatty acids were used (caprylic acid, lauric acid, palmitic acid, palmitoleic acid and stearic acid). Palmitoleic acid esters were prepared according to the protocol described for palmitic acid esters. The crude products contained mostly monosubstituted esters, but also small amounts of disubstituted esters, unmodified oligofructose and unreacted fatty acids. Using reverse phase solid phase extraction, the products were fractionated. MALDI-TOF MS and NMR confirmed the purity (>90% for mono-esters, >80% for di-esters) of the purified fractions (Van Kempen, Boeriu, et al., 2013).

Sucrose monolaurate (≥97%) was obtained from Sigma Aldrich (Steinheim, Germany). Sucrose esters with fatty acid chain lengths C16 and C18 (RYOTO esters S1670 and P1670) were obtained from Mitsubishi-Kagaku Foods Corporation (Tokyo, Japan). Both S1670 and P1670 are crude products. According to the manufacturer, S1670 consist of 75% mono-esters and 25% di-, tri-, and poly-esters. The fatty acids consist for 70% of stearic acid. P1670 consists of 80% mono-esters and 20% di-, tri-, and poly-esters. The fatty acids consist for 80% of palmitic acid. These products were used without further purification.

2.2. Methods

2.2.1. Sample preparation

The esters were dissolved in purified deionized water using a magnetic stirrer. For some of the samples (with fatty acid chain lengths of 16 and 18 carbon atoms) it was necessary to heat (maximally 70 °C) to dissolve the esters. Samples were cooled down to room temperature before starting measurements.

2.2.2. Determination of surface tension

The surface tension of the air/water interface stabilized by the esters was determined with an automated drop tensiometer (ITCONCEPT, Longessaigne, France) and with a profile analysis

tensiometer (Sinterface, Berlin, Germany). All experiments were performed at 25 °C and repeated until sufficient reproducibility was obtained. Reported values represent the average of 2–10 measurements.

2.2.3. Light scattering

The size of the aggregates that were present in the solutions at concentrations higher than the CAC was determined using a Zeta-sizer Nano ZS (Malvern Instruments Ltd, Worcestershire, United Kingdom). The solutions were clear, however to remove dust particles and small amounts of undissolved material that could disturb the measurements, solutions were filtered prior to the measurements using Millipore-Millex GP Hydrophilic PES filters with a pore size of 0.22 μm (Merck Millipore, Billerica, United States). Measurements were performed at 25 °C with three measurements per sample. Reported size distributions represent the average of these three measurements. Measurements were also performed at concentrations below the CAC to verify the absence of the aggregates.

2.2.4. Ellipsometry

The amount of material that adsorbed at the interface was determined using null ellipsometry. We used a Multiskop instrument (Optrel Gbr, Berlin, Germany) with the angle of incidence set at 55°. The light source was a He–Ne laser with a wavelength of 632.8 nm. From the obtained values of the ellipsometrical angles Ψ and Δ, the amount of adsorbed material was calculated using a three-layer model with a dn/dc of 0.15, which is common for small surfactants (Deleu et al., 2013; Stollenwerk et al., 2011; Vacklin, Tiberg, Fragneto, & Thomas, 2005). The variation in the dn/dc value for different materials is small (generally between 0.15 and 0.18) (Stollenwerk et al., 2011) and the actual value of dn/dc does not affect the ratio between the head group sizes that were obtained. Experiments were performed at room temperature at bulk concentrations higher than the CAC. At these concentrations, no significant changes in Ψ and Δ were found in the first 10 min after the start of measurement. This indicates that the interfaces were already saturated. Measurements were performed in duplicate.

3. Results & discussion

In this study, the effect of variations in chemical fine structure on functional properties of oligofructose fatty acid esters was investigated. The esters were prepared by esterifying fatty acids to oligofructose. In all cases, the oligofructose was a mixture of oligomers with a degree of polymerization varying between 2 and 8 (average 4.4). Consequently, the resulting esters are also mixtures (Van Kempen, Boeriu, et al., 2013). The first variation in the structure of the molecule was the length of the fatty acid chain. Four different fatty acid chain lengths were used: C8, C12, C16 and C18. The second variation was the degree of substitution. For all fatty acid chain lengths, the main reaction products mono-esters (one fatty acid per oligofructose molecule), were studied. For the two shortest fatty acid chain lengths (C8 and C12), also di-esters (two fatty acids per oligofructose molecule) were studied. Di-esters of the longer fatty acid chain lengths were not studied due to their limited presence in the crude reaction product and due to their very high hydrophobicity which limited their solubility in water. This very low solubility in water made them unsuitable for the type of experiments that we are interested in. By changing the chemical fine structure of the molecule, the balance between hydrophobicity and hydrophilicity, expressed as HLB value, is changed. The HLB value was calculated according to the method of Griffin (1954). The structural parameters for the esters that were studied are summarized in Table 1.