

The Effect of Diesters and Lauric Acid on Rheological Properties of Air/Water Interfaces Stabilized by Oligofructose Lauric Acid Monoesters

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ABSTRACT: In this study, the rheological properties of interfaces stabilized by oligofructose fatty acid esters were elucidated. First, the properties of interfaces stabilized by monoesters (ME), diesters (DE), lauric acid (LA), oligofructose (OF), and mixtures of ME with DE, LA, or OF were studied. Second, the properties of interfaces stabilized by the crude product (CP) containing ME, DE, LA, and OF were studied. The dependency of the dilatational modulus on frequency and deformation amplitude indicated the possible formation of a soft glass phase for ME, and a viscous interface for DE. When ME and DE were mixed at a ratio of 0.8/0.2, the experimental results suggest that the interfacial structure consists of islands of a glass phase formed by ME, dispersed in a 2D viscous phase of DE. CP stabilized interfaces, where the ratio ME/DE was higher, lead to a different rheological response. The ratio ME/DE plays an important role in the surface properties of the CP. This may have significant consequences for applications in macroscopic systems such as foams.

KEYWORDS: surface tension, surface rheology, air/water interface, food-grade surfactant, sugar ester, mixed interfaces, interfacial microstructure, soft glass

INTRODUCTION

Sugar esters have been the subject of investigation for many years.^{1–3} They are food-grade nonionic surfactants^{4,5} and widely used within the food industry⁶ because they have attractive properties. They are produced from renewable and largely available feedstock⁷ and are biodegradable, nontoxic, odorless, and tasteless.⁸ They can be used for many different applications since they can be produced with a wide range of hydrophobicity. This wide range is accomplished by the use of fatty acids of different chain length, by varying the degree of substitution of the sugar group, and by changing the degree of polymerization of the carbohydrate.

Industrially available sugar esters are often produced by chemical synthesis methods which result in a mix of esters with different degrees of substitution. Also, there are usually traces of fatty acids left behind.^{6,9} When studying the surface properties of these crude samples, it is important to consider the contribution of the different individual components.

By increasing the number of fatty acid chains that are esterified to a sugar group, the surface activity is increased. However, the increased hydrophobicity also leads to reduced solubility. Lower solubility will lead to a slower adsorption at interfaces.¹⁰ Therefore, a higher surface activity is expected for diesters compared to monoesters, as long as the hydrophobicity does not become too high. The hydrophobicity of the molecule is determined by the balance between the size of the hydrophobic and hydrophilic groups.

The contribution of the free fatty acids strongly depends on whether they are able to migrate to the interface, which in turn depends on the amount of monomers that is available in the bulk.

The amount of monomers is strongly influenced by the fatty acid chain length and the degree of saturation, both of which influence the melting point. Below the melting point, the fatty acids will be present in the bulk in the form of insoluble precipitates that will not migrate to the interface. Surfactant micelles can aid in the transportation of fatty acids from bulk to interface below their melting point. Golemanov et al.¹¹ have shown that, by using the anionic surfactant sodium lauryl-dioxyethylene sulfate and the zwitterionic surfactant cocoamidopropyl betaine, in combination with medium chain fatty acids, it is possible to create interfaces with a high dilatational modulus. They hypothesized that mixed micelles of both types of surfactants and fatty acids were formed that transported fatty acids to the interface, where they formed a condensed layer, leading to a high modulus. If a similar mechanism would occur when fatty acids are present in a crude product containing oligofructose fatty acid esters, the fatty acids in the crude product could contribute to the surface properties.

Husband et al.⁶ have studied the surface tension and foaming properties of sucrose lauric acid esters. They studied crude reaction products, purified monoesters, purified diesters, and mixtures of monoesters and diesters. They found a higher surface tension and poorer foaming properties of diesters compared to monoesters. The crude product had improved foaming properties compared to either pure component. Addition of diesters to

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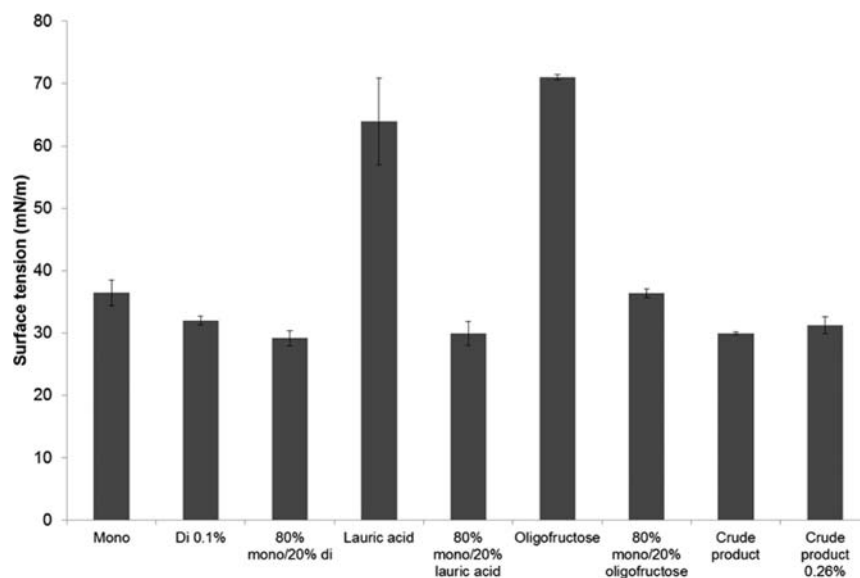


Figure 1. Equilibrium surface tension of air/water interfaces (determined at a bulk concentration of 0.2%, except when stated otherwise) stabilized by purified oligofructose lauric acid monoesters, diesters (0.1%), lauric acid, oligofructose, mixes of monoester with diesters, lauric acid, and oligofructose, and the crude reaction product (at 0.2 and 0.26%). Values represent the mean of 2–7 measurements. The error bars represent the standard deviation.

monoesters improved the foaming properties to that of the crude product. These results demonstrate the importance of understanding not only the contribution of each individual component present in a crude reaction product to the functional properties but also the contribution of mixtures of these components. To the best of our knowledge similar studies, where the effects of different components present in crude products on the functional properties are investigated, are rare.

While synthesis and functional properties of fatty acid esters of mono- and disaccharides are frequently described,^{12–15} reports on oligosaccharide esters are usually limited to the synthesis.^{16–20} Because of their ability to create interfaces with both a low surface tension and a high dilatational modulus, previous research by our group focused on synthesis and functional properties of oligofructose lauric acid esters (OLAE). A study on functional properties showed that crude OLAE could lower the surface tension of an air/water interface considerably and provide a high dilatational modulus. These interfacial properties also translated into high foam stability.²¹ The OLAE are produced by enzymatic esterification of oligofructose to fatty acids. The oligofructose that is used is a mixture of different degrees of polymerization (between 2 and 8). As a result, the oligofructose esters that are obtained are also a mixture of different components. Because of the specific enzymatic reaction procedure, the reaction yields mostly (67%) monoesters (one fatty acid coupled to one oligofructose molecule). However, also small amounts of unesterified oligofructose, diesters (two fatty acids coupled to one oligofructose molecule), and unreacted fatty acids are present.²² After synthesis, the different fractions are separated and purified monoesters and diesters are obtained.

We expect major differences in the functionality of the different pure components (ME, DE, LA, OF). Furthermore, mixtures of these components can have completely different functionality compared to the pure components. Hence, the composition will affect performance of the OLAE in actual applications (such as foam or emulsion stabilization). Therefore, the purpose of this study was to investigate the contribution of the different components present in the crude product, and combinations of these components, to the properties of air/water

interfaces stabilized by OLAE. First, the properties of the purified monoester were investigated. Then, the properties of the other components present in the crude product and a mix of 80% monoester with 20% of this component were studied (diester, lauric acid, and oligofructose). Finally, the properties of the crude product were investigated, and a hypothesis on the interfacial microstructure is proposed to explain the rheological behavior of the different systems.

■ MATERIALS AND METHODS

Materials. Oligofructose with a degree of polymerization (DP) between 2 and 8 (average 4.4) was a kind gift of Beneo-Orafti (Tienen, Belgium). In some cases the oligofructose chain was terminated by a glucose unit. Lauric acid was obtained from Sigma-Aldrich (Steinheim, Germany).

Synthesis. Oligofructose lauric acid esters were prepared according to a previously described protocol.²² The crude product was washed once with *n*-hexane to remove lauric acid. The composition of the product was estimated using MALDI-TOF MS. The composition of the detectable part of the crude product was approximately 67% monoesters, 10% diesters, and 23% unmodified oligofructose. Although the presence of lauric acid could not be verified with MALDI-TOF MS, it is likely that small amounts of lauric acid are present in the crude product. After this, the product was fractionated to separate the different fractions. MALDI-TOF MS and NMR confirmed the high purity (97%) of the purified monoesters.²² For diesters a purity of 90% was obtained. The main impurities were monoesters, but also small amounts of unmodified oligofructose and triesters were present.

Sample Preparation. Samples were prepared by dissolving the surfactant in purified deionized water. All concentrations are expressed as % w/v in the bulk. The total concentration was 0.2% in all cases, except for pure diesters, where, due to low solubility, a concentration of 0.1% was chosen. This concentration is above the critical micelle concentration (determined as approximately 0.003%). The critical micelle concentration of the monoester was approximately 0.23%.

Determination of Surface Tension and Surface Dilatational Modulus. The surface tension and surface dilatational modulus of the air/water interface were determined with a profile analysis tensiometer (Sinterface, Berlin, Germany). The area of the drop was 20 mm². During time sweeps (22 h), sinusoidal oscillations with an amplitude of 5% and a frequency of 0.1 Hz were applied. The experiments consisted of 25 cycles of oscillations that were alternated with 1 cycle of rest. About 1 s

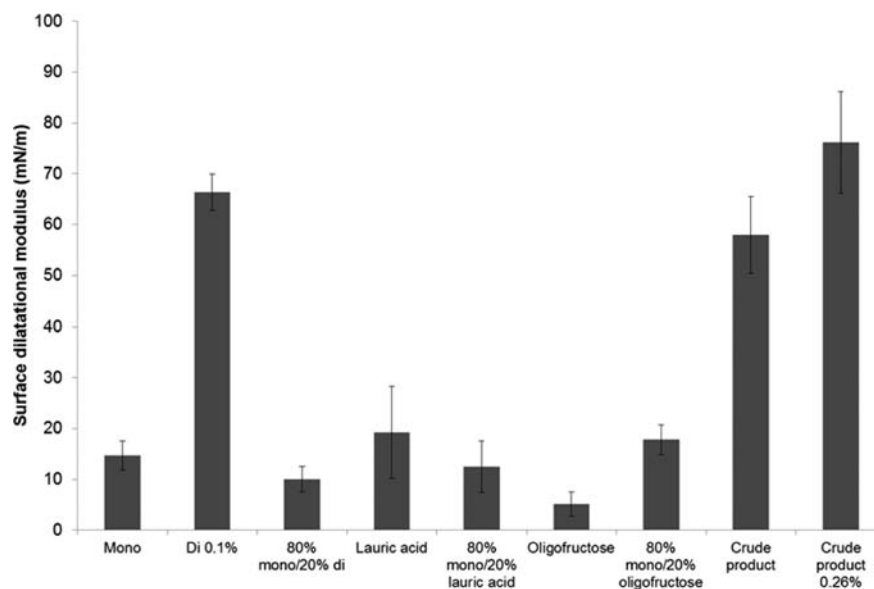


Figure 2. Equilibrium surface dilatational modulus of air/water interfaces (determined at a bulk concentration of 0.2%, except when stated otherwise) stabilized by purified oligofructose lauric acid monoesters, diesters (0.1%), lauric acid, oligofructose, mixes of monoester with diesters, lauric acid, and oligofructose, and the crude reaction product (at 0.2 and 0.26%). Values represent the mean of 2–7 measurements. The error bars represent the standard deviation.

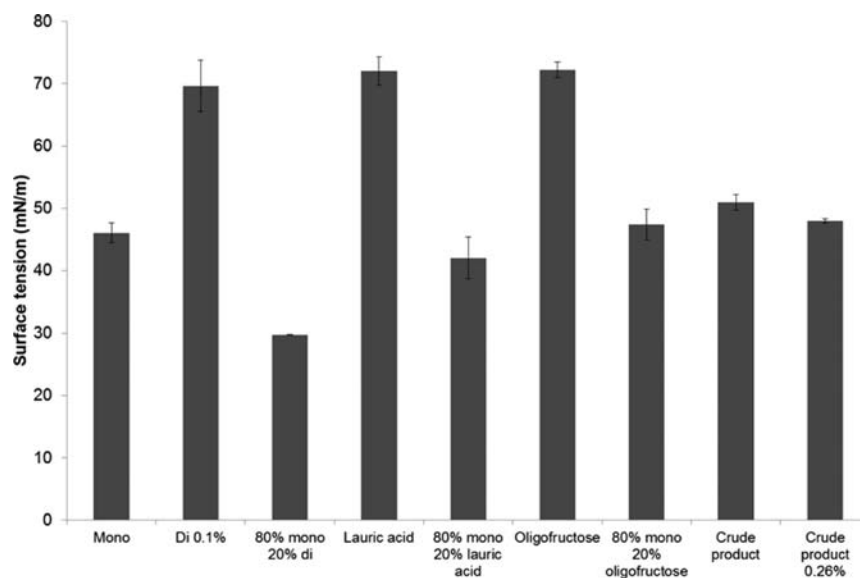


Figure 3. Surface tension 1 s after creation of air/water interfaces (determined at a bulk concentration of 0.2%, except when stated otherwise) stabilized by purified oligofructose lauric acid monoesters, diesters (0.1%), lauric acid, oligofructose, mixes of monoester with diesters, lauric acid, and oligofructose, and the crude reaction product (at 0.2 and 0.26%). Values represent the mean of 2–7 measurements. The error bars represent the standard deviation.

after drop creation the equipment took the first measurement. This value was taken as the initial surface tension used in Figure 3. The time sweeps were followed by a frequency sweep where the frequency was increased stepwise from 0.005 to 1 Hz, at an amplitude of 5%. The slope of a double logarithmic plot of surface dilatational modulus versus frequency was determined using a linear regression fit. Reported values represent the average slope of 2–7 measurements with the corresponding standard deviation. After the frequency sweep, an amplitude sweep was performed where the amplitude was increased stepwise from 1.5% to 30%, at a frequency of 0.1 Hz. The results of the amplitude sweeps are presented in the form of Lissajous plots. We have used the output of the profile analysis tensiometer to construct these plots, of the surface pressure ($\Pi = \gamma - \gamma_0$) versus deformation ($\delta A/A_0$). Here $\delta A = A - A_0$, γ , and A are the surface tension and area of the

deformed interface, and γ_0 and A_0 are the surface tension and area of the non-deformed interface. All experiments were performed at 25 °C. Reported values represent the average of 2–7 measurements.

RESULTS AND DISCUSSION

In this study, the properties of air/water interfaces stabilized by oligofructose fatty acid esters are elucidated. The functional properties of several components present in the crude reaction product (monoesters, diesters, lauric acid, and oligofructose) and mixtures of these components are discussed.

Monoester. At a surfactant concentration in the bulk of 0.2% (w/v), the equilibrium surface tension of an air/water interface stabilized by the purified monoester was 36.5 ± 2.1 mN/m

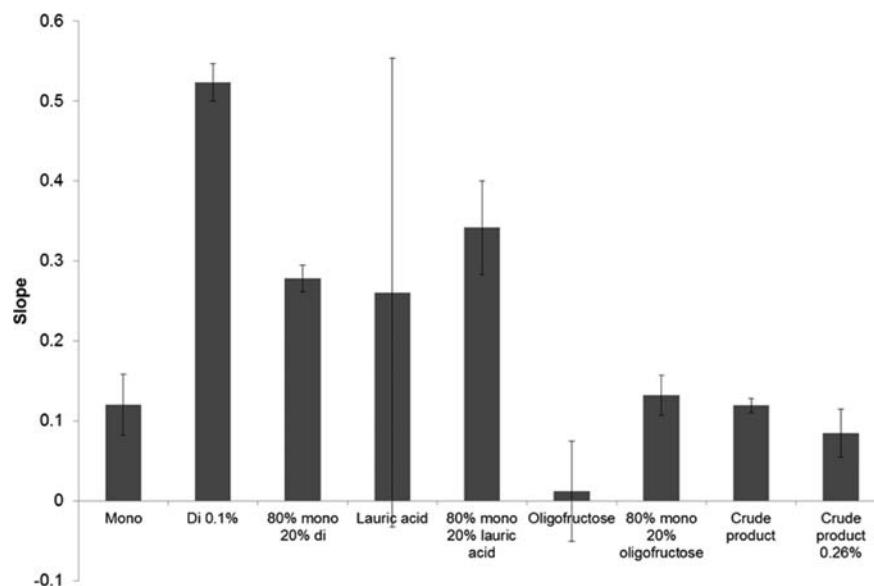


Figure 4. Slope of a double logarithmic plot of surface dilatational modulus versus frequency of air/water interfaces (determined at a bulk concentration of 0.2%, except when stated otherwise) stabilized by purified oligofructose lauric acid monoesters, diesters (0.1%), lauric acid, oligofructose, mixes of monoester with diesters, lauric acid, and oligofructose, and the crude reaction product (at 0.2 and 0.26%). Values represent the mean of 2–7 measurements. The error bars represent the standard deviation.

(Figure 1), while the equilibrium surface dilatational modulus was 14.7 ± 2.8 mN/m (Figure 2). The surface tension after 1 s was 46.0 ± 1.6 mN/m (Figure 3). The fairly fast decrease in surface tension points to a molecule that can migrate to the interface rather rapidly. To gain a deeper understanding of rheological characteristics of the interface, a frequency sweep was performed starting immediately after the time sweep. The slope of a double logarithmic plot of modulus versus frequency was 0.12 ± 0.04 (Figure 4). This value is much lower than the value of 0.5 predicted by the Lucassen–van den Tempel model²³ for low molecular weight surfactants, and points to the presence of a mostly elastic layer. This is further confirmed by the low value of the loss tangent (0.031 ± 0.008). After the frequency sweep, an amplitude sweep was performed. The results are presented as Lissajous plots of surface pressure versus deformation, in a procedure similar to Ewoldt et al.²⁴ (Figure 5A). Here surface pressure was taken as a measure of stress. The figure confirms the elastic nature of the interfacial layer. Furthermore, the curve is asymmetrical. In the compression part of the cycle, the curve becomes more steep with increasing deformation. Hence, the interface is strain hardening upon compression. In the extension part of the curve, the curve becomes less steep with increasing deformation. So the interface is strain softening upon expansion. The low exponent in the frequency dependence of the dilatational modulus combined with the strain hardening observed in compression and strain softening observed in extension are indications that the ME are forming a soft glass phase after adsorption to the interface.²⁵

The critical micelle concentration (CMC) of pure monoesters is around 0.23% (to be published). Since the total concentration of surface active material was 0.2% for the samples in this study, the concentration of monoesters was slightly below the CMC. In the next paragraphs, the monoesters were mixed with other components present in the crude reaction product at a ratio of monoester/other component of 0.8/0.2.

Pure Diester. The equilibrium surface tension of an air/water interface stabilized by the pure diesters (32.0 ± 0.7 mN/m) was lower than the surface tension of an interface stabilized by pure

monoesters (Figure 1). The equilibrium surface dilatational modulus of an air/water interface stabilized by diesters was 66.4 ± 3.6 mN/m and much higher than the one obtained with monoesters (Figure 2). Closer examination of the surface tension after 1 s shows a high surface tension of 69.7 ± 4.1 mN/m (Figure 3). Apparently, the migration of the diester toward the interface is much slower than that of the monoester. This is caused by the higher hydrophobicity of the diester. The analysis of the frequency sweeps reveals a slope of 0.52 ± 0.02 (Figure 4). A slope of 0.5 is consistent with surface processes that are diffusion-controlled, according to the Lucassen–van den Tempel model.²³ The Lissajous plot of surface pressure versus deformation (Figure 5B) reveals that the interfaces stabilized by DE are more viscous than those stabilized by ME. The curves also show asymmetries, but far less pronounced than for ME stabilized interfaces. From the slope of 0.5 in the frequency sweep and the lack of asymmetry observed in the Lissajous plots we conclude that DE stabilized interfaces do not show mesophase formation and behave similarly to interfaces stabilized by simple surfactants, where the dilatational modulus depends on the rate of exchange with the bulk phase. The high modulus is therefore caused by the slow adsorption of DE from the bulk to the interface.

Mix of Monoester and Diester. Both monoesters and diesters adsorb at the interface. However, since the speed of adsorption and the degree of mesophase formation are different for both species, it is important to study the properties of mixed interfaces of both species. Therefore, the surface properties of an air/water interface formed from a mix of monoesters and diesters were studied. The surface tension of an air/water interface stabilized by a mixture of 80% monoesters and 20% diesters was 29.2 ± 1.2 mN/m. This value is slightly lower than the surface tension value obtained with pure diesters (Figure 1). Similar to these results, when studying sucrose esters, Husband et al.⁶ have found that the surface tension of a mix of mono- and diesters was similar to that of the component that led to a lower surface tension, in their case the monoester. Next, the surface dilatational modulus was determined. When oligofructose monoesters and

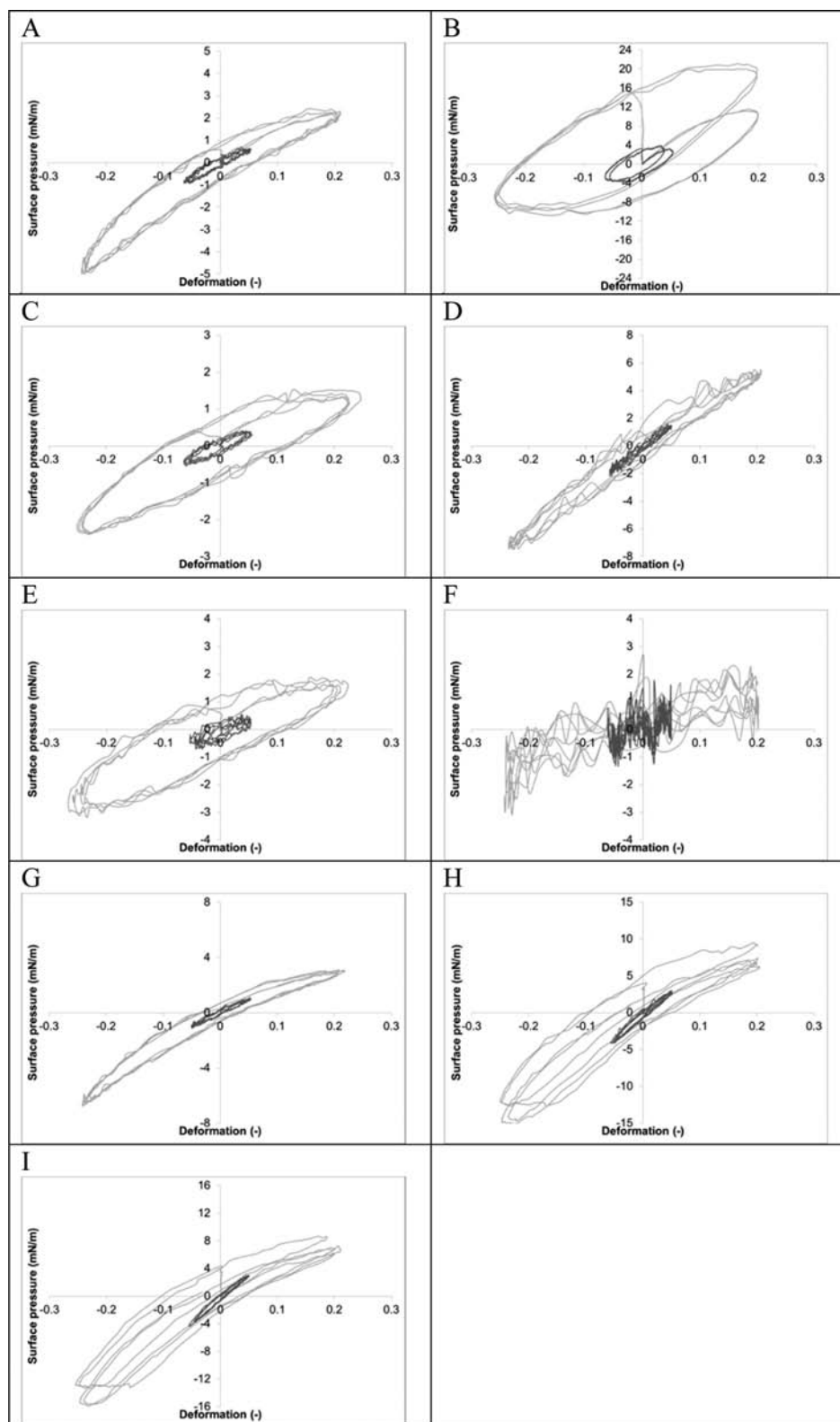


Figure 5. Lissajous plots of surface pressure versus deformation, obtained during amplitude sweeps (determined at a bulk concentration of 0.2%, except when stated otherwise) for monoesters (A), diesters (0.1%) (B), mix of monoesters and diesters (C), lauric acid (D), mix of monoesters and lauric acid (E), oligofructose (F), mix of monoesters and oligofructose (G), crude reaction product (H), crude reaction product (0.26%) (I). Figures show single measurements that were representative for all measurements. During amplitude sweeps, the amplitudes were varied from 1.5% to 30%. For sake of simplicity, only 5% and 20% amplitude are plotted.

diesters were mixed, a surface dilatational modulus of 10.0 ± 2.5 mN was obtained (Figure 2), which is similar to that obtained with the pure monoester. The surface tension value after 1 s was

29.8 ± 0.0 mN/m (Figure 3), which is lower than the value obtained with either pure component. Apparently, the presence of the monoester greatly accelerates the adsorption of the diester.

This acceleration could be the result of the formation of mixed micelles. The analysis of the frequency sweeps reveals a slope of 0.28 ± 0.02 (Figure 4), which points neither to diffusion-controlled processes nor to the presence of an elastic layer. The Lissajous plot (Figure 5C) reveals a more viscous interface than a pure monoester stabilized interface. However, it is still more elastic than a pure diester stabilized interface. Furthermore, there is also an asymmetry in the curve, with slight strain hardening during compression and slight strain softening during expansion. When taking into consideration the surface tension, which was equal to the one obtained with pure diester, combined with the data from the frequency and amplitude sweeps, which point to an intermediate between monoester and diester in terms of interfacial structure, the interfacial structure could consist of islands of a glass phase formed by the monoester, surrounded by diesters. This hypothesis still has to be confirmed by structural analysis.

Pure Lauric Acid. As a result of the synthesis methods, many crude samples of sugar esters contain traces of fatty acids. However, their possible influence on the functional properties is usually neglected.^{6,9} The surface properties of air/water interfaces stabilized by fatty acids strongly depend on the surface concentration and the temperature. The surface concentration of fatty acids depends on their ability to migrate to the interface, which is strongly dependent on the amount of monomers in the bulk phase. Below their melting point, the fatty acids will be present in the form of insoluble precipitates that will not migrate to the interface. At temperatures above the melting point, the insoluble precipitates will disappear and the individual fatty acids will migrate to the interface where they significantly lower the surface tension. Chumpitaz et al.,²⁶ for example, have found a surface tension of 27 mN/m at 60 °C at an air/water interface stabilized by lauric acid. However, a very high dilatational modulus will only be found at temperatures below the melting point when the surface concentration is sufficiently high. In this study, we have determined the surface tension and surface dilatational modulus of an air/water interface at 25 °C to determine if sufficient monomers are present at this temperature to have a significant impact on the functional properties. The equilibrium surface tension obtained for an interface stabilized by pure lauric acid in this study was 63.9 ± 7.0 mN/m (Figure 1). The dilatational modulus was 19.2 ± 9.0 mN/m (Figure 2). These values point to a molecule that did not dissolve well in the bulk phase and therefore did not adsorb at the interface in significant quantities. At equilibrium, the surface concentration of lauric acid was still very low. The surface tension after 1 s, which was 72.0 ± 2.3 mN/m (Figure 3), confirms the poor solubility in the bulk phase. The analysis of the frequency sweeps reveals a slope of 0.26 ± 0.29 (Figure 4), which does not provide useful information due to the large error, which is caused by the extreme scattering in the data for the modulus. The data from the amplitude sweep (Figure 5D) show that the small amount of material that did adsorb at the interface formed a purely elastic layer, which is expected for insoluble fatty acids.

Mix of Monoester and Lauric Acid. Surfactant micelles can facilitate the transportation of fatty acids from bulk to interface at temperatures below their melting point. Golemanov et al.¹¹ have shown that, by using the anionic surfactant sodium lauryldioxyethylene sulfate and the zwitterionic surfactant cocoamidopropyl betaine in combination with fatty acids, it is possible to create interfaces with a high dilatational modulus. To test whether monoesters can have a similar effect in increasing the amount of lauric acid that is transported from bulk to interface,

thus enabling lauric acid to contribute to the interfacial properties, we have determined the surface tension and surface dilatational modulus of an air/water interface stabilized by a mixture of 80% monoesters with 20% lauric acid. The surface tension of an air/water interface stabilized by a mixture of monoesters and lauric acid was 29.9 ± 1.9 mN/m (Figure 1). This value for the surface tension is lower than the surface tension of a pure monoester stabilized interface. Apparently, the presence of monoesters caused an increase in the amount of lauric acid that was present at the interface. This could be the result of the formation of mixed micelles. The surface dilatational modulus of an air/water interface was similar for monoesters, lauric acid, and a mix of lauric acid and monoesters (Figure 2). Apparently, although there was an increase in solubility, the surface concentration of the lauric acid at equilibrium was not high enough to cause an increase in the modulus. Golemanov et al.¹¹ have found a sharp increase in modulus when the surface tension of their system was around 25 mN/m. The fact that the surface tension in our system was higher supports the conclusion that the surface concentration of lauric acid is too low to achieve a high surface dilatational modulus. The surface tension after 1 s (42.0 ± 3.4 mN/m, Figure 3) was similar to the surface tension of a pure monoester stabilized interface, which points to an interface that was initially dominated by monoesters. With time, more and more lauric acid was delivered to the interface, leading to the formation of a more compact interfacial layer, which resulted in a lower surface tension. The fact that this decrease took a much longer time compared to the case of a mixed monoester/diester interface may be attributed to a lower degree of solubilization by the monoesters. Analysis of the frequency sweeps shows a slope of 0.34 ± 0.06 (Figure 4). Like in the case of mixed monoester/diester interfaces, the value of the slope points neither to diffusion-controlled processes nor to the presence of an elastic layer. The analysis of the Lissajous plot (Figure 5E) reveals an interfacial layer with intermediate viscoelasticity, comparable to Figure 5C. There is asymmetry with slight strain hardening upon compression and slight strain softening upon expansion. Similar to the case of a mixed monoester/diester interface, this could be the result of the formation of a mixed layer, consisting of patches of a glass phase formed by monoester surrounded by lauric acid molecules.

Pure Oligofructose. The oligofructose that was used is a mixture of oligomers with different degrees of polymerization, with only hydrophilic parts. As a consequence, the oligofructose is not expected to be surface-active. The lack of surface activity is reflected in the high equilibrium surface tension (70.7 ± 0.2 mN/m) (Figure 1), the surface tension after 1 s (72.5 ± 1.6 mN/m) (Figure 3), and the low dilatational modulus (5.9 ± 1.6 mN/m) (Figure 2). The analysis of the frequency sweeps (Figure 4) and amplitude sweeps (Figure 5F) does not present any useful information due to the lack of surface activity.

Mix of Monoesters and Oligofructose. Since oligofructose is not surface-active, it is not likely that it will affect the surface properties of monoesters. However, for the sake of completeness and to verify the absence of any unforeseen effects, we have determined the properties of a mix of monoesters and oligofructose. The surface tension of an air/water interface stabilized by a mixture of 80% monoesters and 20% oligofructose was 36.4 ± 0.7 mN/m (Figure 1), while the surface dilatational modulus that was obtained (Figure 2) was 17.8 ± 2.9 mN/m. Both values are similar to pure monoesters. The surface tension after 1 s was 47.4 ± 2.5 mN/m (Figure 3), which is similar to the surface tension obtained with pure monoester after 1 s. The

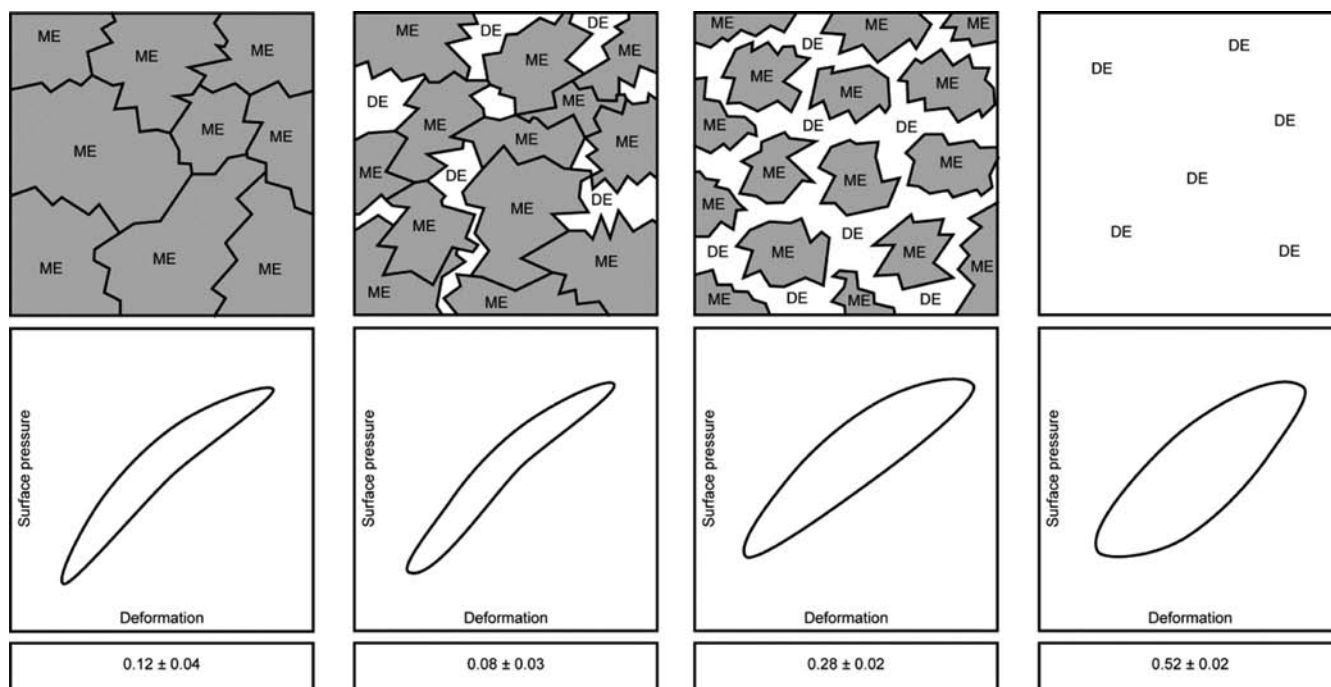


Figure 6. Top row: proposed interfacial structure of OLAE. Middle row: schematic Lissajous plots. Bottom row: Slope of a double logarithmic plot of surface dilatational modulus versus frequency. From left to right: a soft glass formed by pure monoesters, a mixed interface formed at ratio of monoester/diester of 0.87/0.13, a mixed interface formed at ratio of monoester/diester of 0.8/0.2, a pure diester stabilized interface.

analysis of the frequency sweeps shows a slope of 0.13 ± 0.02 (Figure 4), which is the same as the slope of the curve of pure monoester. Finally, the Lissajous plots (Figure 5G) are also similar. Since oligofructose is not a surface active molecule, its only contribution to the functional properties was the diluting of the monoesters, which did not have a significant effect on the functional properties because the concentration was still close to the CMC.

Crude Product. The composition of the crude product was estimated to be around 67% monoesters, 10% diesters, and 23% unmodified oligofructose. The amount of lauric acid was not determined but is not likely to exceed a few percent.^{6,9} Since in previous paragraphs it was established that even at a ratio of monoester/lauric acid of 0.8/0.2 the effect of lauric acid on the functionality was very small, the role of lauric acid in the crude product is expected to be limited. The ratio monoester/diester in this mixture is 0.87/0.13. This means that the relative amount of monoester in the product is higher than in the 0.8/0.2 mixture. Furthermore, the amount of surface active material in the sample is only 78%. The diester has a low CMC of approximately 0.0031% (to be published), so the concentration of diester is still above the CMC. However, the CMC of the monoester is around 0.23% (to be published). With only 67% monoester in the sample at a concentration of 0.2%, the concentration of monoester is below the CMC. The surface tension of an air/water interface stabilized by the crude product was 29.9 ± 0.2 mN/m (Figure 1) and similar to the surface tension of an air/water interface stabilized by the diester alone, and to the mixes of monoester with diester or lauric acid. This value is lower than the surface tension that was obtained in a previous study on oligofructose lauric acid esters (39 mN/m).²¹ Besides the fact that in the previous study the concentration was slightly lower (0.1% compared to 0.2% in this study), it is important to consider that the degree of polymerization of the oligofructose groups and the ratio monoester/diester in both products were not the same.

An air/water interface stabilized by the crude product showed a rather high surface dilatational modulus of 57.9 ± 7.5 mN/m (Figure 2), which is comparable to the modulus of an interface stabilized by pure diesters. The surface tension after 1 s was 50.9 ± 1.3 , which is similar to the surface tension measured for pure monoester. Analysis of the frequency sweep shows a slope of 0.12 ± 0.01 , which is low and similar to the monoester. For most amplitudes, the Lissajous plot (Figure 5H) shows elastic behavior with strain hardening in compression and strain softening in expansion, similar to the pure monoester. However, at higher amplitudes the response becomes more viscous, especially during compression. Concluding, results from the frequency and amplitude sweeps show behavior similar to a system stabilized by pure monoester. However, based on the similarity between the surface tension of interfaces stabilized by pure diester and the crude product, and the fact that the modulus is much higher than for a pure monoester interface, the interfacial structure cannot be similar to that of the monoester. Furthermore, when the amplitude is increased during the amplitude sweep, the modulus decreases while tan delta increases. This points to the formation of a firm elastic structure at the interface, that is sensitive to changes in deformation and is broken down when amplitudes become too high.

Surface properties were also determined for the crude product at a higher bulk concentration of 0.26%. At this concentration, the amount of surface active material is 0.2% and the same as in the previous paragraphs. Therefore, the system can be compared more easily to the mixtures discussed there. There were no major differences between the properties of the crude product at a bulk concentration at 0.2% and 0.26%, as shown in Figures 1–4 and 5I. Therefore, the difference in surface properties between the crude product and the individual components or mixes cannot be attributed to the lower concentration of surface active components in the crude product.

Hypothesis on Interfacial Microstructure. To summarize the findings until now, an interface stabilized by pure monoesters showed a low frequency dependency of the modulus, combined with strain hardening in compression and strain softening in expansion. Also, the modulus was low. We concluded that a soft glass phase must have been present. In contrast, an interface stabilized by pure diesters showed a high frequency dependence corresponding to the Lucassen–van den Tempel model²³ without asymmetries. This is typical simple surfactant behavior. The modulus was high and reflected the slow speed of adsorption. For the crude product with a ratio of monoester/diester of 0.87/0.13, we found an elastic interface with strain hardening in expansion and strain softening in compression and a high modulus. For the mix of monoesters and diesters with a ratio of monoester/diester of 0.8/0.2, we found intermediate frequency dependence and slight strain hardening in expansion and strain softening in compression. This was combined with a low modulus.

There are two hypotheses to explain the differences between the rheological characteristics of the crude product (ratio monoester/diester 0.87/0.13) and the mix of monoester with diester (ratio monoester/diester 0.8/0.2). First, the structure at the CP stabilized interface might be composed of a mixture of monoester, diester, and lauric acid. However, it seems unlikely that this explains the observed difference because the amount of lauric acid in the crude product is rather low. Second, the ratio between monoester and diester might be crucial for the development of the structure at the interface. If the monoester indeed forms a soft glass, it should be quite brittle. This means that the structure can easily be disrupted when the deformation amplitude becomes too high. Indeed, we never observe a linear response regime for the purified ME interfaces. This may explain the relatively low value for the modulus of a pure ME stabilized interface. When the surface fraction of DE increases, the system goes from a soft glass to a dispersion of glassy ME patches in a viscous DE phase. Initially, when the fraction of DE is small, the ME patches still dominate the interface and create an interface that is less brittle, but still elastic with a high modulus. With increasing DE fraction, the amount of glassy ME patches reduces, which leads to a loss of connectivity. Eventually, this leads to a loss of the elastic character and of the high modulus. The proposed mechanism is summarized in Figure 6. Similar results were obtained by Choi et al.²⁷ for phospholipids and by Golemanov et al.²⁸ for saponins. Although a lot of information about the interfacial structure can be gathered from rheological data, it is very important to confirm the hypotheses that were proposed in this article using appropriate methods, such as Brewster angle microscopy, particle tracking observed by microscopy,²⁹ or grazing incidence X-ray diffraction.³⁰

Although they are the main components in the crude product, the surface properties of the product are not solely governed by monoesters. Diesters and free lauric acid, which are often present in crude samples, do contribute to the functional properties. To apply this type of material as a foam or emulsion stabilizer, the effect of other components present in the crude product must always carefully be considered. Small variations in composition may lead to significant changes in functionality.

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Notes

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ABBREVIATIONS

ME, monoester; DE, diester; LA, lauric acid; OF, oligofructose; CP, crude product; OLAE, oligofructose lauric acid esters; MALDI-TOF MS, matrix-assisted laser desorption/ionization time-of-flight mass spectrometry; NMR, nuclear magnetic resonance; CMC, critical micelle concentration

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