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Scanning force microscopy as a tool to investigate the properties of polyglycerol ester foams

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ABSTRACT

Foamed products are a popular class of food products. The mechanism of stabilization of the air bubbles is often only partially understood. The current study aims at better understanding the stabilization of air–water interfaces through the low molecular weight surfactant polyglycerol ester (PGE). We chose PGE films as an exemplary case for a non-equilibrium situation at an air–water interface – a situation that requires the development of new experimental techniques. Several different film preparation and transfer methods onto solid substrates have been tested. The films were then investigated by scanning force microscopy, and structural artifacts associated to the sample preparation were identified and discussed. In addition to the study of Langmuir monolayers and Gibbs adsorption layers, we have proposed a new approach to investigate the skins of foam bubbles. We thereby were able to determine that PGE indeed covers bubbles by a multilayer structure and that the pH plays a role in the structuring of the films. We show that a combination of different film preparation methods allows us to get an insight into the aggregation behavior of PGE at the air–water interface and thereby better understand the stabilization mechanism of this particular surfactant.

1. Introduction

Many food products, such as whipped cream, ice cream, chocolate mousse, sponge cake, and bread owe their unique texture to the large amounts of gas incorporated during the production process. The dispersed gas phase within a foam is generally stabilized by surface-active agents. The main role of such surface-active agents is to prevent the rupture of bubbles by stabilizing the films between them [1]. Three main types of surface-active agents can be distinguished. The first one is the class of low molecular weight surfactants [2,3], such as sodium dodecyl sulfate (SDS), Tween or mono- and diglycerides. The second type of molecules are proteins [4–7] e.g. β-lactoglobulin or bovine serum albumin. As an alternative to the use of molecules, particles can be employed to stabilize air–water interfaces [8–11]. In these three cases the thermodynamic and dynamic characteristics of the surface-active agents are different. Thus the foamability of a solution and the stability of the resulting foam are influenced significantly by the choice of surface-active agent [12].

Many techniques exist to study the characteristics of surface-active agents used for foaming. A comprehensive review on foaming agents and methods to investigate foams was published by Murray [13]. Interfacial rheology both in the shear and dilatational mode is applied frequently to characterize air–water interfaces [14–18]. One can go one step further by combining interfacial shear rheology with Brewster angle microscopy [19]. This allows for the establishment of a direct link of the rheological information to structural changes taking place within the interface. Furthermore, neutron and X-ray reflectivity measurements are used to determine the thickness of films, as well as their internal structure [20,21]. Yet another way of gaining insight into the stabilization of foams is by studying the disjoining pressures of foam films. In these experiments the thinning behavior of one single foam film consisting of two air–water interfaces is investigated [22–24].

Despite the diversity of the methods mentioned so far, they all have the disadvantage of being performed on a model interface. The preparation of these interfaces does not correspond to the way an air–water interface within a foam is created. As an example, the preparation of interfaces to be investigated often requires the dissolution of the surface-active agent in an organic volatile solvent, to allow for spreading of the surfactant onto the interface, followed by the evaporation of the solvent. Even if this will be

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avoided by letting the surface-active agent adsorb from an aqueous bulk solution onto the interface, the convective forces, which are non-negligible in the transport of surface-active agents to the interface in foam production, are not accounted for. For interfacial structures in a thermal equilibrium the history of the film preparation does not play a role. It becomes relevant though for systems, which do not reach thermal equilibrium. Many practically relevant systems, such as protein or particle stabilized films, show structures in a non-equilibrium state. Studying the structures stabilizing air–water interfaces directly within foams though is a challenging task. As an example, foams are turbid, which complicates optical measurements, especially of foam films in the interior of the sample. One possibility of investigating surfactant structures within foams had been shown to be small angle neutron scattering [25,26].

The surface-active agent of interest in the current study is a commercially available PGE. This particular surfactant was chosen as it has been shown to have very good foaming properties [27]. Different structures were found in aqueous solutions of this non-ionic surfactant. The presence of surfactant self-assemblies, such as planar lamellar phases and multi-lamellar vesicles, was observed by electron microscopy and concluded from small angle neutron scattering [28]. Measurements of interfacial tension of dilute solutions at room temperature have shown that the surfactant adsorption is slow, and no true equilibrium in interfacial tension can be reached, even after an adsorption time from the bulk solution to the air–water interface of 4 h [29]. The adsorption kinetics is faster at higher concentrations, with a 1 wt% PGE solution reaching an equilibrium surface tension of 40 mN/m after an adsorption time of approximately 30 min [27]. Using dilute solutions, interfacial rheological studies at the air–water interface have shown a viscoelastic behavior that was discussed as a possible result of a temporary network formed by hydrophobic interactions of the fatty acid chains of PGE. The increase in interfacial storage modulus in adsorbed layers, as compared to spread layers, was hypothesized to be caused by multiple layers adsorbing to the interface [29]. Another point of major interest is the influence of the pH on the behavior of this surfactant. This interest is based on the fact that the foamability of PGE solutions has been shown to be significantly increased at pH 3, as compared to the native pH of the solution (pH 9 at a concentration of $c = 1$ wt%) [27]. Also, binary coalescence experiments have shown that bubbles produced in solutions at pH 7 (native pH of the solution at $c = 0.01$ wt%) are significantly more stable than bubbles in solutions at pH 3 [30].

Adding to the complexity of this system this effect of pH is not well understood. It is also still largely unknown in which structural entities PGE molecules adsorb from the bulk solution to an air–water interface. One open question concerning the adsorption process is whether the vesicles play an active role in it, or whether they disintegrate in the bulk and only single surfactant molecules diffuse to the air–water interface. Also the makeup of the above-proposed network, or in more general terms the structure of the molecular assemblies present at the air–water interface, remains another question. Furthermore, the possible presence of inhomogeneities in the surfactant film might play a significant role in the stabilization of the foam.

The interest to work with a non-pure substance, of which in addition the chemical composition is up to now only rather poorly characterized, is twofold. First of all, to our best knowledge, the used PGE 55 is the only non-ionic low molecular weight surfactant mixture showing such an extraordinary stabilization of foams. In addition its properties have recently been investigated in detail using other techniques [27–30]. Therefore we are convinced that from its properties and behavior one can obtain new insight into foam stability mechanisms, which cannot be obtained from more simple systems. Second, from an application point of view, a pure substance containing only one type of polyglycerol ester would be too expensive and therefore not applicable.

Scanning force microscopy (SFM) allows for the investigation of thin films and their structure, even at conditions relevant for foaming, and also far beyond the resolution of optical microscopes [31]. The goal of the current study was to characterize PGE foams with SFM. In order to get a better understanding of the foam stabilization mechanism of PGE, we have applied several different techniques of preparing the surfactant films. (i) The investigation of Langmuir monolayers allowed us to determine the monolayer thickness. (ii) Measurements performed at the liquid–solid interface gave us new insight into the surfactant adsorption behavior. (iii) We have transferred foam films directly from a bubble onto a hydrophobic substrate, allowing for the investigation of surfactant structures present at air–water interfaces of foams. The ability of transferring thin films from a bubble onto different hydrophobic substrates, while keeping the film intact, had been shown in the literature for Newton Black films [32–34]. In order to characterize the quality of the film and to ensure its integrity, we used a high-speed camera to follow the bubble rupture during film transfer.

2. Experimental section

2.1. Materials

The polyglycerol ester used was the commercially available, food-grade surfactant PGE 55. It was purchased from Danisco (Braband, Denmark) and used without any further purification. It is not a pure substance, but contains predominantly a mixture of esters of di-, tri- and tetraglycerol with the degree of esterification being unknown [28]. The average molecular weight is Mw ≈ 770 g/mol [29], and the product contains about 1.4 wt% free fatty acids, which are residues from the production process [28]. The water used in all the trials was purified with a Millipore purification unit (Millipore) and had a resistivity of 18.2 MΩ cm. A PGE solution with a concentration of 1 wt% has a native pH of 9 [27]. For the experiments performed at pH 3, 1 M HCl (Normapur, VWR) was used for the adjustment. Two types of solid supports were used to study polyglycerol ester films. For all trials, where films were transferred from the air–water interface onto a wafer, air-dried silicon wafers (epitaxial and polished, Siltronic AG) were used. The wafers were rinsed with Milli-Q water and then plasma cleaned (Plasma Cleaner/Sterilizer PDC-002, 200W, Harrick Scientific Corp.) with Argon for 5 min before use. For experiments with hydrophobic wafers, following the cleaning procedure the wafers were placed into a petri dish and a few drops (≈0.25 ml) of octadecyltrichlorosilane (ABCR GmbH & Co KG) were added to the petri dish, without being in direct contact with the wafers. The petri dish was covered with a lid and the octadecyltrichlorosilane was left to evaporate and thereby render the wafers hydrophobic over night. For the measurements performed in liquid, highly ordered pyrolytic graphite (HOPG; SPI-2 grade, SPI supplies) platelets were used.

2.2. Methods

2.2.1. Solution preparation

The PGE solutions were prepared (adapted from [28]) by weighing the respective amounts of surfactant and Milli-Q water into clean glass flasks. These solutions were heated to 80 °C in a water bath and then kept at this temperature for 10 min. During the whole heating process the solutions were stirred using a magnetic stirrer. The solutions were then quiescently cooled in an ice-water bath. Before any experiments the solutions were left to equilibrate