



Surface properties of adsorption layers formed from triterpenoid and steroid saponins



Nevena Pagureva^a, Slavka Tcholakova^{a,*}, Konstantin Golemanov^b, Nikolai Denkov^a, Eddie Pelan^b, Simeon D. Stoyanov^{b,c,d}

^a Department of Chemical and Pharmaceutical Engineering, Faculty of Chemistry and Pharmacy, Sofia University, 1 J. Bourchier Ave., 1164 Sofia, Bulgaria

^b Unilever R&D, Vlaardingen, The Netherlands

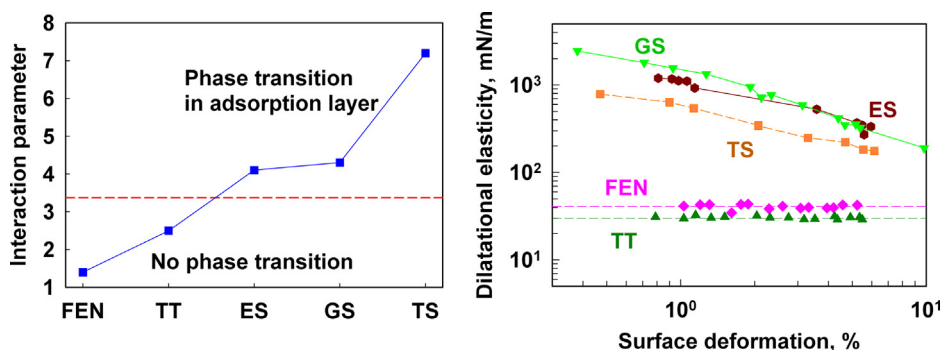
^c Laboratory of Physical Chemistry and Colloid Science, Wageningen University, 6703 HB Wageningen, The Netherlands

^d Department of Mechanical Engineering, University College London, Torrington Place, London WC1E 7JE, UK

HIGHLIGHTS

- Layers of Tea Saponin, Escin and Berry saponins exhibit visco-elastic behavior.
- These layers have very high viscosities and elasticities under dilatational and shear.
- Visco-elastic behavior is due to the strong attraction between the saponin molecules.
- These saponins form surface condensed phases in their adsorption layers.
- Experimentally measured elasticities are close to the theoretically calculated ones.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 5 November 2015

Received in revised form

29 November 2015

Accepted 1 December 2015

Available online 2 December 2015

Keywords:

Surface rheology

Dilatation

Shear

Saponins

Air–water interface

ABSTRACT

Saponins are natural surfactants with non-trivial surface and aggregation properties which find numerous important applications in several areas (food, pharma, cosmetic and others). In the current paper we study the surface properties of ten saponin extracts, having different molecular structure with respect to the type of their hydrophobic fragment (triterpenoid or steroid aglycone) and the number of sugar chains (1 to 3). We found that the triterpenoid saponins Escin, Tea Saponin and Ginsenosides have area per molecule in the range between 0.5 and 0.7 nm², and the adsorbed molecules are orientated perpendicularly to the interface. The comparison of the experimentally measured surface elasticities with theoretically estimated ones shows that the saponins with very high dilatational and shear elasticities (up to 2000 mN/m) have molecular interaction parameter in the adsorption layers which is above the threshold value for two-dimensional phase transition. In other words, the highly elastic layers are in surface condensed state, due to strong attraction between the adsorbed molecules. Furthermore, these adsorption layers have non-linear rheological response upon expansion and contraction, even at relatively small deformation. Layers from the other studied saponins (steroids and crude mixtures of triterpenoid saponins), which are unable to form strong intermolecular bonds within the adsorption layer, have zero shear elasticity and viscosity and low dilatational elasticity and viscosity, comparable in magnitude to those reported in literature for protein adsorption layers. The comparison of the results, obtained by several independent experimental methods, allowed us to formulate the conditions under which the results

* Corresponding author. Fax: +359 2 962 5643.

E-mail address: SC@LCPE.UNI-SOFIA.BG (S. Tcholakova).

from different interfacial rheology tests could be compared, despite the complex non-linear response of the saponin adsorption layers.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction and aim of the study

Saponins are a class of natural surfactants found in more than 500 plant species [1–3]. Due to their amphiphilic nature saponins have strong surface activity. The adsorption layers of some saponins exhibit visco-elastic behavior in shear [4–6] or in dilatational deformation [7–9]. It is known that foams with higher surface modulus are generally more stable to Ostwald ripening, [10,11] bubble coalescence [12,13] and foam drainage [10,14]. The magnitude of the surface modulus impacts also the rheological properties of bulk foams [15]. Saponins have a number of positive bio-effects [1,3,16,17]: anti-fungal, anti-bacterial, anti-cancer [18,19], cholesterol-lowering [20,21], anti-oxidant, anti-inflammatory [22], etc. Their unique surface and biological properties make them a very good choice for foam stabilizers in practical application: food, cosmetics, and pharmaceuticals.

In our previous study [7] we showed that triterpenoid saponins from *Quillaja saponaria* formed adsorption layer with area per molecule, $A \approx 1 \text{ nm}^2$ in which the molecules lay parallel to the air–water interface with the hydrophilic glucoside tails protruding into the aqueous phase. Upon small deformation, these adsorption layers exhibit very high surface dilatational elasticity ($280 \pm 30 \text{ mN/m}$), much lower shear elasticity ($26 \pm 15 \text{ mN/m}$), and negligible true dilatational surface viscosity. We showed that the measured dilatational elasticity is in a very good agreement with the theoretical predictions of Volmer adsorption model (260 mN/m).

In another study [6] we characterized the rheological behavior of adsorption layers of 11 different saponin extracts, subjected to creep–recovery and oscillatory shear deformations. These experiments showed that all steroid saponins exhibited no shear elasticity and had negligible surface viscosity. In contrast, most of the triterpenoid saponins showed complex visco-elastic behavior with extremely high shear elastic modulus (up to 1100 mN/m) and shear viscosity (130 N s/m). The saponin extracts, showing the highest elastic moduli, were those of Escin, Tea saponins and Berry saponins, all containing predominantly monodesmosidic triterpenoid saponins. Similarly high surface modulus was measured with Ginsenosides extract, containing bidesmosidic triterpenoid saponins with short sugar chains.

The current study is dedicated to the relation between the molecular characteristics of the adsorption layers, determined from surface tension isotherms, and the surface rheological behavior of the same systems, subjected to dilatational and shear deformations. To achieve our aim we measured the surface tension isotherms for different saponin extracts and analyzed them by van der Waals and Volmer model isotherms. The rheological characteristics of the adsorption layers, subject to shear deformation, are taken from our previous study [6], whereas the characteristics of adsorption layers under dilatational deformation are measured for the current study using two experimental techniques: Capillary pressure tensiometry (CPT) and Langmuir trough (LT). Experiments were performed in oscillatory (CPT, LT) or steady deformation (LT). There are relatively few publications on dilatational rheology of saponins [7–9], and they are focused exclusively on one particular system (*Quillaja saponin*). As far as we know, this is the first systematic study of the characteristic behavior in surface dilatation of different types of saponins.

A study of this kind is important in another aspect as well. As already mentioned, results published in the literature show specific trends about the relation between surface and bulk properties in foams. However, in some cases, rigorous explanations of these trends are still missing. It is not yet clear which characteristics of the adsorption layer, shear or dilatational (or both), are relevant to the dynamics of a particular dynamic process in foams (Ostwald ripening, bubble coalescence, viscous friction, etc.). Detailed information of the behavior of the systems both in dilatation and in shear deformation is essential for the understanding of these relations. Such knowledge would ultimately help in the selection and utilization of saponins for stabilization of foams and emulsions.

2. Materials and methods

2.1. Materials

Table 1 provides information on the studied saponins: abbreviations used in the text, suppliers, concentration of saponins in each extract. Additional information for studied saponins such as part of the plant which was processed is given in Table S1 in Supporting information. Fig. S1 presents the basic molecular structure of the saponins, isolated from each extract.

2.2. Method for measurement of surface tension

The Wilhelmy plate method [23,24] was used to determine the equilibrium surface tension, σ_e , of the solutions. The measurements were performed on a K100 tensiometer (Kruss GmbH, Hamburg, Germany) by using a platinum plate. Before each measurement, the plate was cleaned by heating on a flame, followed by abundant rinsing with deionized water. The experiments were performed at constant temperature of 20°C .

2.3. Experimental techniques for the characterization of surface rheological properties of adsorption layers

Two different experimental techniques were applied to characterize the surface rheological and adsorption/desorption behavior of the adsorption layers. Capillary pressure tensiometry (CPT) was performed via DSA 100 automated instrument (Kruss GmbH, Germany). The CPT method allows one to calculate the surface tension, σ , after measuring the capillary pressure difference, P_c , across the surface of a spherical drop with a radius of curvature of R [25–28]. The elastic and viscous moduli were determined from harmonic surface oscillations of spherical drops. First, a drop was formed, the surface was left to age for 30 min, and then the experiment was performed. A sinusoidal variation of the drop surface area, A , is applied, with a defined angular frequency, ω (the respective oscillation period is $T = \omega/2\pi$), and amplitude, ΔA . Simultaneously, one measures the resulting variations of the surface tension, σ . From the relation between $\sigma(t)$ and $A(t)$ we determined the complex surface modulus $E^* = E' + iE''$ (here i is the imaginary number) and E' and E'' are the surface storage (elastic) and loss (viscous) moduli, respectively. The values of E' and E'' were obtained using the linear regression procedure, described in Ref. [27]. All experiments were performed at constant frequency of oscillation (0.1 Hz) and constant temperature (20°C).

Download English Version:

<https://daneshyari.com/en/article/591792>

Download Persian Version:

<https://daneshyari.com/article/591792>

[Daneshyari.com](https://daneshyari.com)