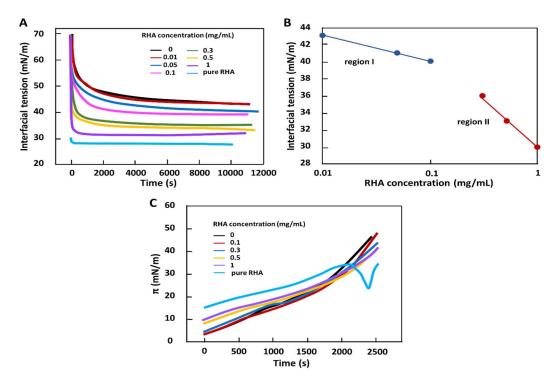
How surface tension measurements can help to find new foaming agents.



Foams are a widely used shape in which cosmetics and pharmaceuticals are applied due to a good spreading ability and their lack of stickiness. Nowadays, cosmetic manufacturers are eager to provide their products in foam form, because consumers consider foamlike cleaning products are of higher quality with better usability. Surfactants, as the main component of washing cosmetics, achieve foaming by quickly and effectively reducing the surface tension. Compared with synthetic surfactants, natural biological substitutes (biosurfactants) have attracted more and more attention in body care and bath cosmetic fields due to their low toxicity and inherent biodegradability. Rhamnolipid (RHA) is one of these biosurfactants which is produced by bacteria such as *Pseudomonas aeruginosa*. RHA has a considerably lower standard Gibbs free energy of adsorption and micellization, therefore RHA can form micelles much more easily than synthetic surfactants. However, surfactants are often not enough to ensure the stability of the foam, and other components like proteins are necessary to improve the stability. Though many studies on the mixture of protein and biosurfactants have been conducted, the synergistic or antagonistic effect of protein addition on the foaming properties of biosurfactants still needs to be solved. Recently Wang and coworkers have studied the interaction between soybean protein (SP) and RHA proposing a possible correlation between surface behavior and actual foaming properties.

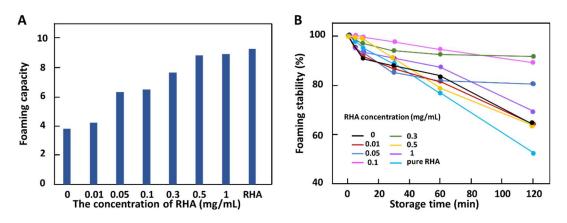
In order to understand the interaction between soybean protein and RHA in solution and to demonstrate the interfacial stabilization of aqueous foam based on SP-RHA interacting mixture it was first needed to quantify how many RHA molecules bind to each soybean protein. An isothermal titration calorimetry measurement revealed that each SP can bind to more than 28 RHA molecules forming a SP-RHA complex, and that the two molecules have a high affinity mainly due to hydrophobic interaction. To study the interface adsorption of SP/RHA/water mixtures with different ratios, dynamic interface tension measurements were conducted by using an optical contact angle analyzer. The surface tension of SP-RHA complexes/water mixtures decreased over time during the absorption process of SP-RHA at the interface (liquid/air) and then kept constantly which indicates the interface was saturated with SP-RHA (Picture 1A). At a low RHA concentration (0.01 mg/mL), the decay curve almost maintained unaffected in which case SP predominated the dynamic interface tension. When the RHA concentration was increased (from 0.05 to 0.5 mg/mL), the decay curves differed from that of pure SP/water mixtures and the decline rate gradually increased with lower equilibrium interface tension. When the RHA concentration was 1 mg/mL, the decay curve was similar to that of a pure RHA/water mixture.



**Picture 1:** A) Dynamic interface tension of SP/RHA/water mixtures with different RHA concentrations (0-1 mg/mL) as a function of time; B) Interface tension after 180 min of adsorption as a function of RHA concentration; C) Surface pressure ( $\pi$ ) of SP/RHA/water mixtures with different RHA concentrations (0–1 mg/mL) as a function of time

In addition the interfacial tension of SP/RHA/water mixtures was compared after 180 min of adsorption (until equilibrium state) to demonstrate its relationship with the RHA concentration. This lead to the identification of two distinct regions of decay curves (**Picture 1B**). In both regions, the surface tension diminishes when the RHA concentration increases. Most probably the SP-RHA complex has a higher activity and dynamics than pure SP. However, the decline rate of region II was much faster than that of region I. They reasoned that the SP binding sites were saturated and excess RHA was available to reduce the surface tension. In a next step they compressed the surface with a Langmuir experiment increasing the surface pressure which resulted in an increased stiffness of the surface film. As shown in **Picture 1C**, the surface pressure at the air-water interface stabilized by the SP-RHA complex over time provided information of the molecular interaction under equilibrium. For the pure RHA, the curve exhibited a quick drop at high surface pressures, representing the rigid and brittle monolayer formed which easily collapses. However, the supplement of SP prevented the surface film from collapse, and they attributed the phenomenon to an order assembly triggered by SP.

In order to evaluate the foaming ability and stability, they measured the maximum foam volume of different samples (**Picture 2**).



**Picture 2:** The foaming properties of SP-RHA complex with different RHA concentrations while SP was 1 mg/mL. A) Foam volume as a function of the RHA concentration; B) Foam volume as a function of time

**Picture 2A** reveals the pure SP sample possessed the smallest foaming volume, indicating the weakest foaming ability, because of the compact structure of SP and thus slower interface adsorption. Upon the addition of RHA, even at very low concentration (0.05 mg/mL), the foaming volume was much higher. As the RHA concentration further increased (from 0.05 to

0.5 mg/mL), the foaming ability progressively improved. These results show that the addition of RHA helps to soften the protein structure and makes SP adsorbed and unfolded at the airwater interface more easily. **Picture 2B** shows the foaming volume changes over time (also termed foaming stability), and they found that the pure RHA had the best foaming ability but poor foaming stability. The foams had their highest stability for RHA concentrations between 0.1 and 0.3 mg/mL. It can be assumed that in this case, SP absorbed at the interface and prevents destabilization by crosslinking into a protein film. Then RHA incorporated into the SP film and made it more flexible and stable against bubble coalescence or burst. Nevertheless, due to the preferred adsorption of free RHA at the interface, a further RHA concentration increase would make it unstable.

In summary, the authors explained the possible correlation between surface behavior and foaming properties by assessing the interaction between SP and RHA in water and the dynamic interface tension of different SP/RHA/water mixture as well. All the results verified that SP-RHA complexes adsorb and orderly assemble at the air-water interface, thus dramatically improving the foaming ability and foaming stability. This research provides ideas to combine proteins and biosurfactants for foaming processes with excellent characteristics and holds considerable promise for foaming applications in food and cosmetic industry.

An optical contour analysis system OCA (DataPhysics Instruments GmbH, Germany) was used in this research.

For more information, please refer to the following article:

Interfacial stabilization of aqueous foam based on soy protein-rhamnolipids interacting mixture; Qi-Jun Ruan, Meng-Ping Wang, Yuan Zou, Chen Lin, Da-Chuan Cai, Jin-Mei Wang; *Industrial Crops & Products* **2020**, 153, 112587; DOI: 10.1016/j.indcrop.2020.112587