Interfacial Rheometry and the Stability of Foams and Emulsions

Keywords: Interfacial shear modulus, Du Noüy ring, protein adsorption, surfactants, stability, foams, emulsions RH018

SCOPE

Interfacial rheology provides information on the adsorption behavior and interactions of molecules at interfaces, which is important for the application and processing of many materials including foods, beverages, pharmaceuticals, cosmetics, coatings, etc. The rheology at the interface is a key element when studying the stability of foams and emulsions. Immiscible fluids (liquids or gas) can be formulated into a product only by stabilizing the interface surrounding the dispersed droplets or bubbles against coalescing or fusing.

There are two major classes of surface active molecules used to stabilize interfaces:

1. Low molecular weight materials such as surfactants, lipids, emulsifier, etc.
2. Proteins, large complex molecules with high molecular weight.

The stabilization mechanism for the two classes of molecules is very different and interfacial rheology is an excellent tool to evaluate the stabilization capabilities of different types of material systems. In foods, such as dairy products, beer, etc., proteins and surfactants or lipids are commonly present. Due to the incompatibility of the two stabilization mechanisms lipids, when adsorbing to protein-stabilized interfaces, disrupt the protein network causing instability of the food foams or emulsions [1].

With the interfacial option based on the Du Noüy ring method for the Discovery Hybrid Rheometer, the development of interfacial layers under varying conditions as well as the resulting stabilization performance can be studied.

MECHANISMS FOR STABILIZATION OF INTERFACES

Liquid-liquid or liquid-gas interfaces are not static; they are constantly subject to external disturbances which result in continuous com-pression, stretching and consequently the creation of new interface. Because of the high mobility in the liquid phase, surfactant molecules diffuse very fast to the newly created interface to reestablish the dynamic equilibrium. The fast moving surfactant molecules drag surrounding fluids molecules along – thus filling the inter-lamellar space between droplets i.e. bubbles to keep the separated and prevent coalescence or fusion [2] (Figure 1). This mechanism of stabilization is referred to as Gibbs-Marangoni mechanism and is the key stabilization effect for surfactant molecules. Impurities in fluids behave like surfactants and are responsible for undesired foaming during processing. The absence of the Gibbs-Marangoni effect is the main reason why pure fluids do not foam.

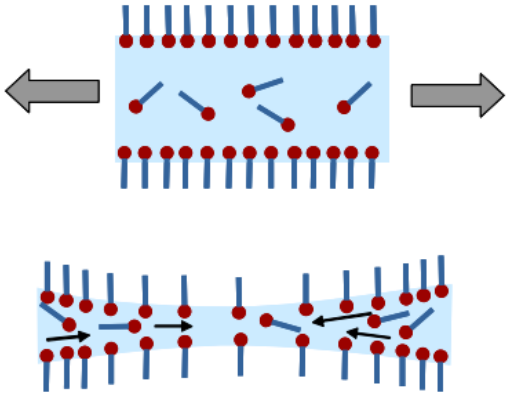

Figure 1: Interface stabilization mechanism with surfactants

If a liquid contains proteins instead of surfactant molecules, the proteins are adsorbed at the interface because of their amphiphilic character, start to unfold and develop strong interactions with neighboring molecules to create a two dimensional viscoelastic gel [3]. This gel exhibits a high elastic shear modulus as a result of the physical network formation (Figure 2). It is the mechanical strength of these protein films, which stabilizes the interface and resists deformation and prevents the film to collapse.

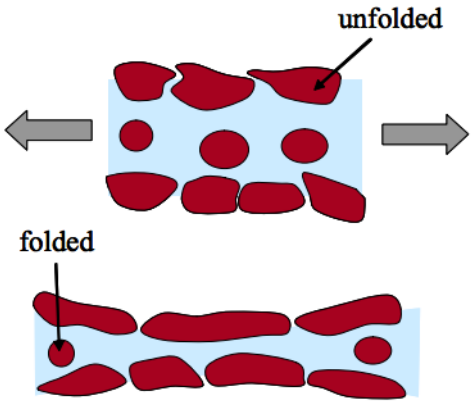

Figure 2: Interfacial stabilization mechanism with proteins

STABILITY OF EMULSIONS AND FOAMS IN THE FOOD INDUSTRY

Many real systems and virtually all food products comprise both, surfactants or lipids and proteins that compete for space at the interface. Foam density measurements show that the foam stability decreases with increasing concentration of surfactant on protein stabilized systems. By adding a surfactant (Tween 20) to a ß-lactoglobulin solution,

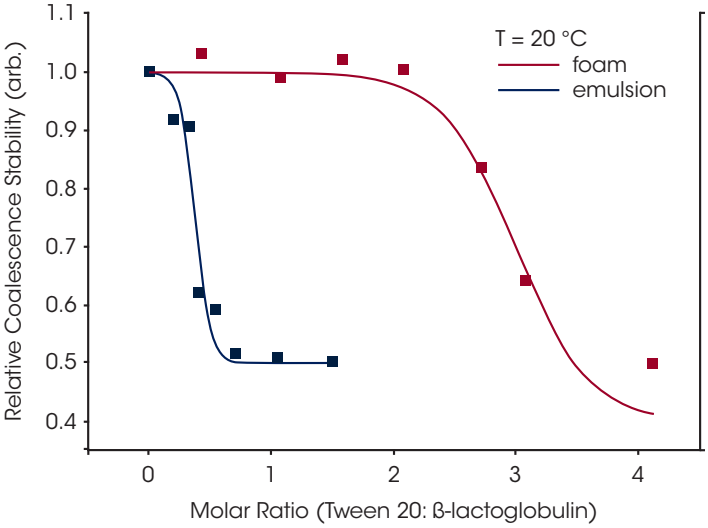

Figure 3: Foam and emulsion relative stabiliy as a function of surfactant (Tween 20). The liquid content measured after 5 minutes drainage time is used to calculate the relative foam stability

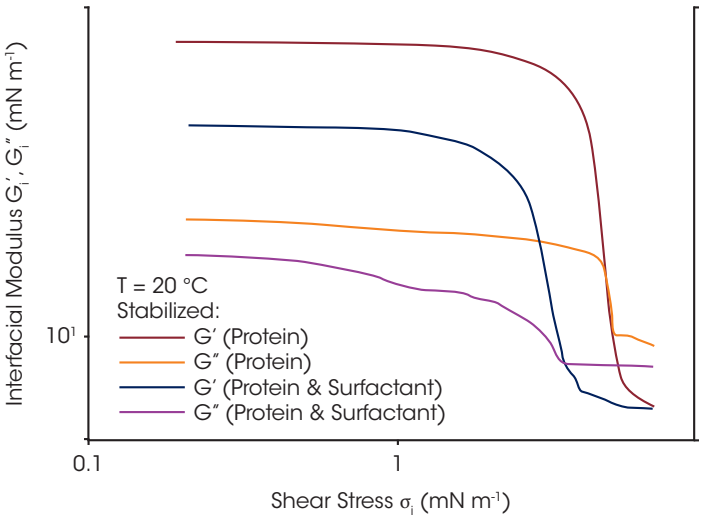

Figure 5: Interfacial shear modulus as a function of stress for protein stabilized interfaces with and without surfactant

the relative stability of the foam decrease with increasing surfactant concentration in Figure 3 [4]. Also increased coalescence is observed for an oil/water emulsion, stabilized with ß-lactoglobulin.

The kinetics of the adsorption of the ß-lactoglobulin and the surfactant tween 20 at the water surface has been monitored measuring the surface shear viscosity at different concentrations of surfactant using the Noüy ring method [4]. With no surfactant present, the complex shear viscosity increases and reaches a plateau value after 100 minutes (Figure 4). The decrease of the modulus at longer times is probably due to impurities such as lipids which act as surfactant, slowly destabilizing the film.

With increasing surfactant concentration, the interfacial shear viscosity increases initially and drops to a lower value later. The maximum in the viscosity decreases and shows earlier as the surfactant concentration increases. These

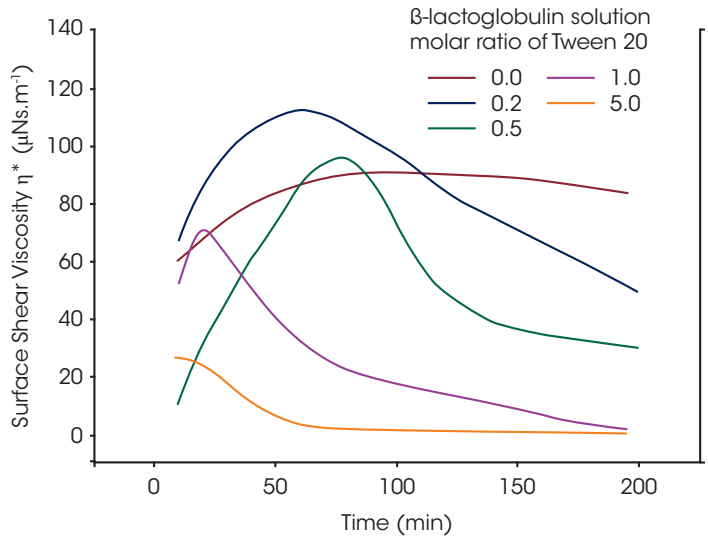

Figure 4: Surface shear viscosity development with time as a function of the surfactant concentration [4]

experimental findings clearly indicate a destabilization of the interface with increasing surfactant concentration.

In order to evaluate the viscoelastic response of the interface, the shear modulus can be separated in its elastic (interfacial storage modulus G'_i) component and its viscous (loss modulus G''_i) component. The separate elastic and viscous components for a pure protein and a mixed protein/surfactant stabilized interface, as a function of applied stress are shown in figure 5. For both solutions, the elastic modulus dominates at low stresses. It is the elastic restoring force, which is responsible for the stability of the foam and emulsion. With surfactant present, the modulus is strongly reduced. With increasing stress, the storage modulus decreases and eventually a cross-over point occurs. The viscous component dominates now and the interface stabilization disappears. This is obvious, as more force is applied to the interface, it will break down eventually. It is not surprising that the cross over point is much higher for the solution with protein only. In foams, the rate of drainage of a liquid past the interface is a low stress phenomenon, vigorous mixing of the foam or emulsion involves much greater stresses at the interface, resulting in a breakdown of the elastic modulus and a drop in stability.

An explanation for this behavior at mixed protein surfactant interfaces is following:

- During the formulation of the emulsion or the foam, the protein is adsorbed at the interface and slowly unfolds to build a gel. The small surfactant molecules, although moving faster, are hindered by the larger proteins; as such their mobility is restricted and the surfactant stabilization effect (Gibbs-Marangoni mechanism) is strongly reduced.

- With time, the surfactant molecules penetrate the protein gel, disrupt the strong interactions of the gel and weaken the network strength. The emulsion or foam resistance to external disturbances and the life time are strongly reduced.

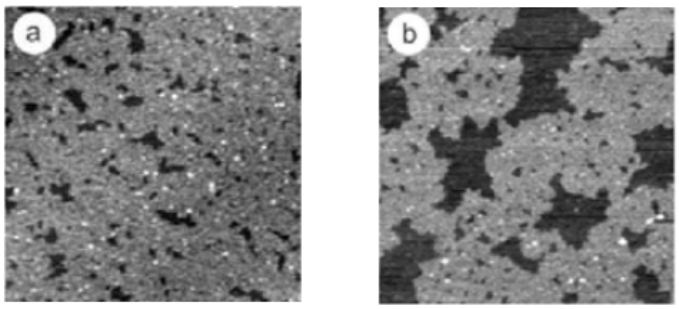

Figure 6: AFM images (1x1 µm) of the competitive displacement of ß-lactoglobulin by Tween 20 at the air/water interface [1]. Surface pressure a) 18.6 mN/m; b) 20.2 mN/m. Dark areas is the space occupied by the surfactant

Figure 6 shows a series of AFM images of the displacement of the ß-lactoglobulin film by Tween 20 from an air-water interface as a function of surface pressure [1]. With increasing surface pressure more surfactant adsorbs at the interface. At low surface pressure, the surfactant (dark areas) appears to randomly displace the protein. With increasing surface pressure, the small holes in the protein network increase in size until the protein network fractures. Detailed analysis suggests, that the protein is compressed, but remains at the interface until the network ruptures. With further expansion of the surfactant domains, the thickened protein film is pulled away from the surface, freeing the protein to move back into the liquid phase.

CONCLUSIONS

The stability of foams and emulsions depends strongly on the chemical composition. Low molecular weight surfactant molecules and high molecular weight proteins adsorb at the interface and stabilize the interface by very different mechanisms. At mixed interfaces, typically in food products, both types of molecules compete with each other. The result is not a better stabilization, but a net destabilization of the foam or the emulsion.

As such beer produces a nice "head on the glass" as long as the glass has not been rinsed previously with a soap solution – thus enhancing the retention of the foam.

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