Interfacial rheology of emulsifiers in food
Stability and sensory properties of emulsions and foams
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Proteins and lipids are the key surface-active substances for emulsions and foams in the food industry. The structure which they form on an oil/water interface influences the stability of foams and emulsions and can even alter the sensory perception of food colloids such as these. Interfacial rheological measurements are often used to examine the interfacial structure of emulsions and foams. We carried out measurements on oscillating pendant drops to determine the viscoelastic modulus of three different, modified food emulsifiers. The samples differ particularly in terms of their elastic modulus $E'$ and lie within a range of 20 to 110 mN / m. The use of the Oscillating Drop Module – ODM, which was newly developed in 2018, in combination with the ADVANCE software means that these key parameters could be determined with particular ease, speed and precision.

Background information
Dilative interfacial rheology describes how interfaces respond to their area changing (increasing / reducing). This reaction can be elastic or viscous and, accordingly, there are the parameters viscoelastic modulus $E$, elastic modulus $E'$ and viscous modulus $E''$, which are typically determined by means of interfacial rheological measurements. In experimental terms, these parameters can be determined using the Oscillating Drop Method [1, 2].

A previous application report provides detailed information about the fact that these measured values have proven very beneficial in practice with regard to optimizing the effectiveness of demulsifiers in the field of crude oil production, for example [3].

A look at the literature (see [4] and the references quoted therein) demonstrates how valuable knowledge of these parameters can be for food technology:

- How does a whey protein form a gel at increased temperatures?
- What surface-active substances stabilize the oil droplets in emulsions best under flow conditions?
- How do proteins need to be modified to minimize destabilization processes in emulsion and foam, such as Ostwald ripening / disproportionation?
- Can the sensory perception of emulsions – in the form of “creaminess”, for example – be correlated with a measurement parameter?

Dilative interfacial rheology was used to examine these and other questions. From an experimental standpoint, however, this had not been very easy up until now, which discouraged many potential users from using the method despite it being highly beneficial. Below, we show how interfacial rheological measurements can be performed on food systems in a precise and simple way with the ODM, which was newly developed in 2018, in conjunction with the ADVANCE software. That way, this powerful analytical method will become accessible to a wider range of users.

Experimental section
We received three different samples for examination from a customer, which straight before the measurement were prepared as aqueous solutions according to the use (Table 1). All three samples are typical, surface-active additives in food. Hydrolyzed protein is used as a flavour enhancer and in products suitable for allergy sufferers. Quillaia extract is used in non-alcoholic beverages to support the foam properties, while propylene-glycolicalginate is present as a thickener, emulsifier or foam enhancer in the likes of water ice, sauces or beer.

Tab. 1: Overview of samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ingredient</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Hydrolyzed protein</td>
<td>20 %</td>
</tr>
<tr>
<td>2</td>
<td>Quillaia extract (E 999)</td>
<td>1 %</td>
</tr>
<tr>
<td>3</td>
<td>Propylene glycolicalginate (E 405)</td>
<td>2 %</td>
</tr>
</tbody>
</table>

The Oscillating Drop Method was used to determine the viscous modulus $E''$, elastic modulus $E'$ and viscoelastic modulus $E$ [1, 2]. To this end, the sample was drawn into a glass syringe, which was used in a Drop Shape Analyzer – DSA100 in combination with an Oscillating Drop Module – ODM. The automatic detection and coupling of the syringe plunger and the high degree of automation that the ADVANCE software permits enable both high precision and excellent repeatability of measurements.

A pendant drop of a well-defined volume was automatically created for the measurement. When the surface tension (SFT) equilibrium value was reached, the drop volume was also oscillated sinusoidally (Fig. 1). The surface in mm² and the SFT were measured on the oscillating drop in parallel. $E$, $E'$ and $E''$ were then calculated from this data. All of this was done automatically using the ADVANCE software.
The measurements were performed at frequencies of 0.5, 1.0, and 3.0 Hz and at amplitudes (deformation relative to the initial area) of 3.6% and 4.8% (data not shown). Frequency and amplitude variations such as these, which would have been complex previously, are easily to access with the help of ADVANCE software. Ten consecutive oscillation periods were carried out per drop and used for the evaluation.

Results

Equilibrium SFT values of 37.8, 35.5 and 53.4 mN/m were determined for samples 1, 2 and 3. A graph comprising surface and SFT data during oscillation is shown by way of example for sample 1 in Fig. 2. The ADVANCE software permits direct review of the raw data (blue), by graphically mapping the adjusted sine functions of the area (yellow) and SFT (red) in parallel. In the example shown, the recorded data is fully described by the adjusted sine functions, so the raw data curves are hard to identify under the congruent sine graphs.

The results for $E'$ and $E''$ are summarized in Figures 3a and 3b. The error bars correspond to the standard deviation resulting from two single measurements and are smaller than the corresponding symbol in most cases. This high level of reproducibility is indicated by the ODM and its high degree of automation for the measurements.

In all three samples, the elastic component dominates the interfacial rheological behaviour ($E' > E''$). While none of the samples in the frequency range examined show any change in the elastic modulus, they differ from one another quite clearly, whereby sample 2 with approximately 100 mN/m has the highest value and sample 3 with approximately 20 mN/m has the lowest value. $E''$ declines for all three samples as the frequency increases.

The results are very informative for use in food production. A quotient comprising the elastic modulus and SFT of $E'/\sigma = 2.8$ can be calculated for sample 2, for example. According to a model by Kloek et al., in the case of quotients $E'/\sigma > 1$ the initial bubble size distribution can be well stabilized in foam, for example, and the decomposition process of Ostwald ripening can be slowed down significantly or even stopped [5]. In accordance with this, substances with a high quotient, like sample 2, are very well suited to stabilizing foams in the food industry.

Finally, it is worth noting that all of the measurements mentioned here were taken within the space of roughly two and a half hours. The possibility of being able to determine these key metrics quickly, easily and with a high level precision is now opening up to users who previously shied away from interfacial rheological examinations because of the high effort involved.
Summary
Interfacial rheological parameters play a key role in the stabilization and sensory modification of food foams and emulsions. With the new Oscillating Drop Module – ODM in combination with the ADVANCE software, these key metrics can be determined with extreme ease, speed and precision, as we demonstrated using the example of three common additives for food colloids. The possibility of measuring over a wide frequency and amplitude range, the simple and intuitive measurements, and the high degree of automation which the hardware and software enable together, permit comprehensive characterization of interfaces – and not just in the food industry, either.

Literature