Doctoral Thesis

Transport phenomena in rotating membrane processed W/O/W emulsions

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Multiple emulsions are emulsions within emulsions. These systems offer a wide range of possible applications for food, cosmetics, or pharmaceutical industries, especially for the encapsulation and the controlled release of active ingredients.

The present work deals with the production of multiple emulsions under gentle conditions by a rotating membrane (ROME) device, with the objective to obtain a high yield of the inner water phase and encapsulated substances. Thus prepared multiple emulsions of water-in-oil-in-water (W/O/W) type are utilized to observe water transport across an oil layer using different rheological methods. The influence of several parameters such as osmotic gradient and surfactant concentration is investigated.

To gain more insight into the water transport mechanisms across an oil layer, the well-defined system of a model double emulsion droplet formed at a double capillary is used. Different transport mechanisms causing differences in transport rate are discussed within this thesis.
Transport Phenomena in Rotating Membrane Processed W/O/W Emulsions

A dissertation submitted to
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for the degree of
Doctor of Sciences

presented by
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Switzerland
The wide world is all about you: you can fence yourself in, but you cannot for ever fence it out.

J.R.R. Tolkien, *The Lord of the Rings*
An dieser Stelle möchte ich den unzählige Leuten danken, die mich im Laufe meiner Dissertation auf die eine oder andere Weise unterstützt haben:

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Lenzburg, im Mai 2010
Muriel Graber
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# Notation

## Latin Letters

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<thead>
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<th>Symbol</th>
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### Greek Letters

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<td>limiting deformation for the LVE range</td>
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<td>$\rho$</td>
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<td>$\sigma$</td>
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<td>$\tau_c$</td>
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<td>yield stress</td>
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<tr>
<td>$\phi$</td>
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<td>volume fraction of the dispersed phase</td>
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<td>$\Omega$</td>
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# Indices

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# Dimensionless Numbers

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<td>$Ca_{crit}$</td>
<td>critical Capillary number</td>
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<td>We</td>
<td>Weber number</td>
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### Abbreviations

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<th>Abbreviation</th>
<th>Definition</th>
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<tbody>
<tr>
<td>CLSM</td>
<td>Confocal Laser Scanning Microscopy</td>
</tr>
<tr>
<td>CMC</td>
<td>Critical Micelle Concentration</td>
</tr>
<tr>
<td>CPDN</td>
<td>Controlled Pore Distance Nano</td>
</tr>
<tr>
<td>CSR</td>
<td>Controlled Shear Rate</td>
</tr>
<tr>
<td>CSS</td>
<td>Controlled Shear Stress</td>
</tr>
<tr>
<td>HLB</td>
<td>Hydrophilic-Lipophilic Balance</td>
</tr>
<tr>
<td>IFT</td>
<td>Interfacial Tension</td>
</tr>
<tr>
<td>LMVT</td>
<td>Lebensmittelverfahrenstechnik (Laboratory of Food Process Engineering)</td>
</tr>
<tr>
<td>LVE</td>
<td>Linear Viscoelastic</td>
</tr>
<tr>
<td>NaCl</td>
<td>Sodium Chloride</td>
</tr>
<tr>
<td>O/W/O</td>
<td>Oil-in-Water-in-Oil Emulsion</td>
</tr>
<tr>
<td>PGPR</td>
<td>Polyglycerol Polyrincinoate</td>
</tr>
<tr>
<td>ROME</td>
<td>Rotating Membrane Emulsification</td>
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<tr>
<td>SFO</td>
<td>Sunflower Oil</td>
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<td>W/O/W</td>
<td>Water-in-Oil-in-Water Emulsion</td>
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Abstract

Water-in-oil-in-water (W/O/W) multiple emulsions consist of oil droplets in an aqueous surrounding containing even smaller water droplets inside the oil. These systems offer a wide range of possible applications for food, cosmetics, or pharmaceutical industries, especially for the encapsulation and the controlled release of active ingredients. The production of multiple emulsions has to be performed under mild conditions in order to obtain a high yield of the inner water phase and encapsulated substances.

The first part of this work deals with the production of multiple emulsions performed by rotating membrane device. Rotating membrane (ROME) emulsification, in comparison to a continuous rotor/stator process, was shown to be quite gentle and, therefore, a suitable process in order to reduce loss of inner aqueous phase during the production to a minimum.

A highly viscous emulsion system containing a high proportion of water (i.e. low fat content) is of considerable interest in food or cosmetics industries. Such a system was produced by ROME with addition of an electrolyte to the inner aqueous phase. The thus induced osmotic gradient led to water transport in direction of the inner water droplets, causing a depletion of the continuous aqueous phase and a consequential viscosity increase. This swelling process is discussed in this work. The influence of various parameters on the swelling and the subsequent breakdown was analyzed using two different rheological methods. The lipophilic emulsifier PGPR has a key role in preservation of the inner water droplets during the multiple emulsion production as well as in stabilization of the new interface generated by the growth of internal water droplets.

The partial superposition of swelling and breakdown complicates the identification of a single parameter’s influence on the diffusion process. Therefore, the second part of this work is concerned with processes at the oil/water interface and with water transport mechanisms studied at model double emulsion drops. Interfacial tensions and interfacial dilatational moduli of the simplified system shed light on the impact of electrolyte and surfactant on the properties of the interface. Spontaneous emulsification was studied at a simple oil/water interface using light microscopy.
To investigate water transport across an oil layer in a well-defined system, model double emulsion droplets were formed at a purpose-built double capillary. Two different situations had to be considered: diffusion across an uniform oil layer of several µm thickness and diffusion across a partly thinned oil film, the latter leading to a strong increase in diffusion rate of more than an order of magnitude. The two transport mechanisms causing these different transport velocities are discussed within this thesis.

**Keywords:** double emulsion, multiple emulsion, NaCl, osmotic gradient, PGPR, rotating membrane, spontaneous emulsification, swelling-breakdown, water transport, W/O/W.
Zusammenfassung


Im ersten Teil dieser Dissertation wird gezeigt, dass die rotierende Membran ein vielversprechendes Verfahren zur Produktion von multiplen Emulsionen darstellt. Im Vergleich mit einem kontinuierlichen Rotor/Stator-Prozess schnitt die rotierende Membran deutlich besser ab, vor allem wenn innere Emulsionen mit hohem Dispersphasenanteil weiter dispergiert wurden. Solche hohen Anteile an innerer Wasserphase sind aufgrund des resultierenden tiefen Fettgehalts oder der hohen Aufnahmekapazität für zu verkapselnde Substanzen oft erwünscht.


Der Einfluss verschiedener Prozessparameter auf das Anschwellen und die darauf folgende Koaleszenz wird in dieser Dissertation ebenso diskutiert, wie die Schlüsselrolle des lipophilen Emulgators PGPR. Dieser schützt nicht nur die Wassertropfen vor der Freisetzung während des Emulgierprozesses, sondern stabilisiert
Zusammenfassung

auch die durch die Diffusion neu entstehende Grenzfläche und führt so zu höher viskosen Produkten. Eine Überlagerung des Anschwellprozesses mit der bereits einsetzenden W1-W2-Koaleszenz erschwerte jedoch eine genaue Identifikation der Wirkung einzelner Inhaltsstoffe und Prozessparameter.


1 Introduction

Multiple emulsions, i.e. emulsions of emulsions, generally are produced in a two step procedure. First a simple emulsion is made, then the inner emulsion is dispersed into an outer continuous phase. Due to their potential for encapsulation and release of substances, multiple emulsions have promising applications in food, cosmetic, and pharmaceutical industries, as well as in separation processes [1, 2].

In conventional turbulence based emulsification processes such as rotor/stator devices or high-pressure homogenizers, high shear forces are applied to disrupt droplets in order to achieve emulsions with small average droplet diameters [3]. Consequently, the very high volumetric energy input may cause the destruction of shear or temperature-sensitive ingredients, such as proteins. Due to the repeated droplet rupturing, considerable amounts of inner phase might leak to the continuous phase during the multiple emulsions production, resulting in a substantial loss of encapsulated substance. Therefore, conventional methods are only suitable to a limited extent for the production of multiple emulsions.

It is known that the membrane emulsification technique is a suitable method to produce these multiple emulsions [2], as only mild stresses are applied to the system. Membrane emulsification, however, is not very suitable for industrial applications, due to its dependency between droplet size and flow rate, and the resulting need for recirculation. Schadler and Windhab [4] introduced a rotating membrane (ROME) device in pilot-plant scale that enables variation in droplet size by adjusting the rotational speed of the cylindrical membrane. This setup allows the production of emulsions with high dispersed phase fractions without recirculation of the continuous phase. In this work, the advantages of the ROME device for the production of multiple emulsions at pilot-plant scale levels are investigated.

Multiple emulsion systems are thermodynamically unstable, and usually a large part of the internal phase is lost during production or storage. For certain applications, however, such as drug delivery, this instability might be desired in order to achieve a controlled release of encapsulated substances [5, 6]. In this thesis, multiple emulsions of W/O/W type with electrolytes dissolved in the inner aqueous phase are produced by a rotating membrane device. The electrolyte leads to a
'swelling-breakdown' process where the continuous aqueous phase diffuses through the oil phase and causes a swelling of the internal water droplets. The subsequent breakdown, i.e. the coalescence between internal water droplets and the continuous phase, causes a release of encapsulated substance. Due to the swelling and the depletion of the continuous phase, a multiple emulsion of medium to very high viscosity and a high proportion of enclosed water is generated. With long term stability proved satisfying, such a system is of considerable interest in cosmetics or food industries. In this work, the influence of important parameters (such as surfactant or electrolyte) on swelling-breakdown, rheological properties, and on the stability of the multiple emulsion system is investigated.

The major difficulty arising from the study of transport processes in multiple emulsion systems is the superposition of swelling and breakdown, making it impossible to investigate the influence of one single parameter on the diffusion process. To obtain a better understanding of the parameters involved in the swelling-breakdown of W/O/W double emulsion systems, the focus in the second part of this thesis was laid on processes at and close to the interface.

The lipophilic emulsifier PGPR has a key role in preservation of the inner water droplets during the multiple emulsion production as well as in stabilization of the interface generated during swelling. Therefore its influence on the interfacial properties as well as its function in the water transport process across the oil film is of interest. The presence of electrolyte is known to have an influence not only on the osmotic gradient but also on the interfacial layers [1]. The electrolyte might compete for water molecules against the surfactant at the oil-water-interface resulting in a rigid interfacial film and hindering the transfer of water or change emulsion stability [7–9].

To study water transport across an oil layer in a well-defined system, model double emulsion droplets were formed at a purpose-made double capillary. Two different situations had to be considered: diffusion across an uniform oil layer of several µm thickness and diffusion across a partly thinned oil film, the latter leading to a strong increase in diffusion rate of more than an order of magnitude. Transport mechanisms causing these different transport velocities are discussed within this thesis.
2 Background

2.1 Rotating membrane emulsification

Crossflow membrane emulsification is a technique for the controlled production of well defined droplets with narrow droplet size distributions. The dispersed phase is pressed through the pores of a membrane and forms droplets on the membrane surface. These droplets are detached and carried off by the continuous phase flowing across the membrane. Due to the mechanism of droplet formation and detachment rather than droplet breakdown, membrane emulsification is considered as emulsification process with low energy consumption. A limiting factor is the quite low disperse phase flowrate. Especially if small droplets are targeted high shear and thus high continuous phase flow velocities are required. Therefore, recirculation is necessary in order to achieve reasonable phase ratios. Considering an industrial scale up the rotating membrane emulsification addresses this problem. The shear forces detaching the droplets from the pores are generated by the rotation of the membrane. Therefore the droplet detachment and the size of the newly formed droplets are decoupled from the continuous phase flow rate.

2.1.1 Membrane emulsification

Conventional emulsification processes as rotor/stator systems or high pressure homogenizers are mainly turbulence based. These processes use high shear in order to deform and disrupt droplets until the desired diameter is achieved. Therefore high energy inputs are required to reduce droplet size, and as a consequence, shear sensitive ingredients such as proteins may be destroyed. Cross flow membrane emulsification on the other hand is a droplet generation method, causing only minimal energy dissipation. It is therefore a suitable method for the production of emulsions containing ingredients sensitive to heat or shear, as well as for multiple emulsions.

In crossflow membrane emulsification the continuous phase passes through a tubular microporous membrane. The to-be-dispersed phase is forced from the outside of the tube through the membrane pores into the continuous phase. Each single
droplet is formed at a pore, its growing surface immediately covered by surfactant molecules present in the surrounding continuous phase. Eventually, the droplets are detached due to the shear flow caused by the continuous phase. The earlier a droplet is detached, the smaller its resulting diameter. A variation in the flowrate of the continuous phase therefore leads to a change in droplet size. As the phase ratio is determined by the flowrate as well, the need for recirculation may arise to achieve more concentrated emulsions.

**Influencing factors.** Parameters influencing the emulsification process and therefore the resulting drop size are divided in three groups. Membrane properties (i) are the size [10, 11] and shape [12] of the pores, the porosity of the membrane [13], and the membrane surface properties [13, 14]. Process parameters (ii) include the crossflow velocity of the continuous phase [15], the transmembrane pressure [16], and the dispersed phase flux [17]. Material properties (iii) are the characteristics of the two phases, e.g. viscosities [18], densities, and polarities, as well as the concentration and characteristics of the surfactant used for emulsification [15, 19].

The membrane emulsification process was reviewed by several groups [16, 20, 21], also with focus on food emulsions [22] or with regard to the generation of multiple emulsions [2]. Further details on the fundamentals of membrane emulsification can be found in the thesis by Schröder [23].

### 2.1.2 Rotating membrane emulsification

The concept of rotating membranes was first developed for applications in membrane filtration. Both, rotating disks and cylinders were used in the context of dynamic filtration [24, 25]. To overcome the limitations of cross-flow emulsification, such as the dependency between flow velocity of the continuous phase and resulting droplet size, Schadler and Windhab [4] used a rotating cylindrical membrane for the continuous emulsion production. In this rotating membrane process the shear forces detaching the droplets were generated by the rotation of the membrane. The size of the emulsion droplets could be varied by the rotational speed. The flow of the continuous phase in axial direction only served the purpose of removing the droplets from the shear gap. A change in phase volume fraction between 5% and 30% of dispersed phase, adjusted by a variation in continuous phase flow rate, did not change the resulting droplet size. To avoid coalescence during droplet formation at the membrane surface, a coated nickel membrane with controlled pore distance and pore diameters of 1 µm was utilized. The influence of Taylor vortices occurring in the annular gap of the rotating membrane geometry
was investigated, as well as the impact of the gap width [26].

Vladisavljevic and Williams [27] studied the rotating membrane concept using a stainless steel membrane with laser drilled pores of 100 µm diameter. They produced emulsions with droplet sizes considerably smaller than the pore size, remaining strictly in the laminar flow regime. Under certain conditions, the formation of daughter droplets (also known as satellite droplets) was observed. Aryanti et al. [28] used the same stainless steel membrane setup, investigating the influence of disperse phase flux on droplet size and uniformity, as well as the impact of different surfactants.

Müller-Fischer et al. [29] used a rotating membrane setup for foam formation. They compared a rotating membrane device to an inverse setup, where in an outer, cylindrical static membrane an inner cylinder is rotating. This dynamically enhanced static membrane showed similar results to the rotating membrane. Compared to a rotor/stator device, the membrane devices led to an improved foam microstructure at a considerably lower volumetric energy input. For both systems, foams and emulsions, no further breakup of droplets once detached from the pores was found [26, 29, 30].

Stillwell et al. [31] used a lab scale inverse setup to produce emulsions of W/O and O/W type. They used a simple paddle-blade stirrer to induce shear at the membrane surface, and were thus able to produce emulsions with a narrow droplet size distribution.

2.1.3 Drop formation and detachment in cross-flow

Forces acting on a droplet. In order to make predictions concerning the emulsion resulting from the membrane emulsification process, it is important to know the forces acting on a droplet forming at a pore (Fig. 2.1). These forces can be divided in two groups: (i) forces retaining the droplet at the pore, and (ii) forces detaching the droplet from the pore. The interfacial tension force $F_\sigma$ is the main retaining force during droplet formation. The static pressure difference force $F_{SP}$, a detaching force, is caused by the pressure difference between dispersed and continuous phase at the membrane surface. Main detaching force is the viscous drag force $F_D$, induced by the flow of the continuous phase in parallel to the membrane. Further detaching forces are dynamic lift force $F_L$, caused by the laminar velocity profile, inertial force $F_I$, induced by the mass of the dispersed phase flowing out of the pore, and the buoyancy force $F_B$, which occurs due to the density difference between dispersed and continuous phase (the latter being not necessarily a detaching force) [17, 23, 26, 30, 32, 33].
To predict droplet breakup in laminar shear flow, the dimensionless Weber number $W_e$ (Eq. 2.1) is defined as the ratio of disruptive forces to forces preserving the droplet. If $W_e$ exceeds a critical value $W_{ecrit}$, droplet breakup occurs.

$$W_e = \frac{\tau d_{drop}}{4 \sigma}$$  \hspace{1cm} (2.1)

with $\sigma$ being the interfacial tension, $d_{drop}$ the droplet diameter, and $\tau$ being the shear stress. Analogous to the Weber number, a dimensionless Capillary number $\text{Ca}_{detach}$ for the detachment of the droplet from the capillary was defined [26]. This Capillary number (Eq. 2.2 and 2.3) includes the above mentioned viscous drag force $F_D$, the interfacial tension force $F_\sigma$, the dynamic lift force $F_L$, and the static pressure difference force $F_{SP}$.

$$\text{Ca}_{detach} = \frac{F_L + F_{SP} + F_D}{F_\sigma}$$ \hspace{1cm} (2.2)

which, according to Eisner [26], leads to the following equation:
2.1 Rotating membrane emulsification

\[ Ca_{\text{detach}} = \frac{d_{\text{drop}}}{d_{\text{pore}}} + \frac{d_{\text{drop}} \tau_w d_{\text{drop}}}{\eta_{\text{cont}} \sigma} \left( 1 + \frac{\sqrt{\tau_w \rho_{\text{cont}}}}{\eta_{\text{cont}} \pi} d_{\text{drop}} \right) \]  

(2.3)

where \( d_{\text{pore}} \) is the diameter of the pore, \( \eta_{\text{cont}} \) the viscosity and \( \rho_{\text{cont}} \) the density of the continuous phase, and \( \tau_w \) the wall shear stress. Therefore, the Capillary number \( Ca_{\text{detach}} \) includes the Weber number for droplet breakup, plus additional terms considering the influence of the pore geometry.

**Microfluidics.** In microfluidics, the flow of small amounts of fluids on the microscale is studied using purpose-built microdevices. To investigate multi-phase flow (intending the formation of multi-phase systems such as emulsions, multiple emulsions or foams) a wide variety of micro-channel geometries were manufactured using different materials and techniques [34, 35].

Membrane emulsification usually has been investigated by evaluating the impact of changing a single material or process parameter on the final product. In doing so, a thorough understanding of the drop formation process could not be achieved. In order to get insight into the influence of single material or process parameters such as flow rate, viscosity ratio or interfacial tension on the mechanism of drop formation and detachment, microfluidic T-flow channels can be used as a model device [36]. Thereby a channel carrying the continuous phase is met by a second channel carrying the to-be-dispersed phase at a T-shaped junction. There, as in membrane emulsification, the to-be-dispersed phase forms droplets into the cross-flowing continuous phase. Due to the transparency of the chip containing the microchannel, the drop formation process may be studied using a high-speed camera.

**Drop detachment in microfluidic T-flow.** Using microfluidic T-Flow channels, several groups [37, 38] investigated the influence of a variation in shear on the droplet size. An increase in shear, caused either by increasing cross flow velocity of the continuous phase or by increasing viscosity ratio, led to earlier drop detachment and consequently smaller drop sizes. Husny and Cooper-White [37] studied the drop formation process as a function of the disperse phase elasticity. While for Newtonian fluids the formation of monodisperse droplets was observable, elastic fluids of equivalent density and interfacial tensions led to the formation of elongated filaments between subsequent droplets. These filaments eventually resolved into small secondary drops, also known as satellite droplets as observed by Vladisavljevic and Williams [27] in rotating membrane produced emulsions (see p. 5). In microfluidic T-flow, the number and viscosity of these secondary droplets
were dependent on the viscosity ratio between the two fluids, whilst the elasticity
determined their presence or absence. The secondary droplets provide an explana-
tion for the bimodal distributions often found in rotating membrane emulsification.

Another important factor in drop formation is the surface wettability. While
a hydrophilic membrane leads to a successful formation of oil drops, the addition
of cationic surfactants, resulting in a wetting of the membrane surface with the
oil phase, inhibits a regular drop formation [15]. According to Xu et al. [38] a
controlled drop formation is only possible if the contact angle between membrane
and dispersed phase exceeds 90° (Fig. 2.2). This illustrates the importance of an
appropriate choice of membrane for the production of an emulsion, depending on
the nature of the dispersed phase.

![Figure 2.2: Effect of wetting properties on droplet formation in membrane emul-
sification. [39–41]](image)

**From pore to membrane.** As the pore network of a membrane is very com-
plex, the simplifying assumption of a system composed of many identical, non-
interacting pores is frequently made. In reality, the interaction between droplets
forming at neighboring pores play an important role. Too small distances between
2.2 Multiple emulsions

Multiple emulsions were mentioned for the first time by William Seifriz in 1925 [43]. Since then, a wide range of work on multiple emulsions dealing with production, stability, and release of encapsulated substances has been published. Nevertheless, many challenges in the field are not yet entirely resolved. Multiple emulsion systems, just as simple emulsions, are thermodynamically unstable, thus a large part of the internal phase usually is lost during production or storage. For certain applications such as drug delivery this instability may be desired [5, 6, 44].

Figure 2.3: Schematic illustration of a water-in-oil-in-water (W1/O/W2) emulsion (a), and an oil-in-water-in-oil (O1/W/O2) emulsion (b).

Multiple emulsions are termed emulsions of emulsions, i.e. they consist of larger dispersed droplets containing smaller inner droplets. There are two main types, on the one hand the water continuous water-in-oil-in-water (W1/O/W2) emulsions, on the other hand oil-in-water-in-oil (O1/W/O2) emulsions where the lipophilic substance is the continuous phase (Fig. 2.3).
2 Background

2.2.1 Stability

The thermodynamic instability of emulsion systems results from the excess free energy at the interface between two phases of different polarity. The cohesive forces between molecules within the individual phases exceed the adhesive forces between the two phases. The larger the interface, the higher the interfacial free energy, and the more thermodynamically unstable the system. The change in interfacial free energy can be expressed by the following equation:

\[ dG = \sigma \, dA \] (2.4)

where \( G \) is the interfacial free energy, \( \sigma \) is the interfacial tension, called surface tension if one of the phases is a gas, and \( A \) is the interfacial area. The high interface in multiple emulsion systems leads to thermodynamical instability, the system aims to reduce the interface by various destabilizing mechanisms eventually leading to a complete phase separation. Main breakdown mechanisms which are known to occur in W/O/W multiple emulsions are coalescence and loss of inner water droplets due to diffusion to the continuous phase [45–49]. A combination of both mechanisms, diffusion and coalescence also leading to destabilization of multiple emulsions is known as 'swelling-breakdown' (Fig. 2.4). Coalescence may take place between two or more oil droplets, between two or more inner water droplets [50], or between inner water droplets and the continuous water phase [51]. The latter case is sometimes referred to as 'bursting', i.e. a rupture of the oil layer and the consequential loss of the entrapped water [52, 53].

Surfactants. The interfacial tension defined by the interfacial free energy \( G \) can be considerably reduced by the addition of surfactants. A surfactant - short for surface active agent - is an amphiphilic molecule, i.e. a molecule containing both hydrophilic a hydrophobic groups. Surface active agents can be classified in two main categories: low-molecular weight surfactants and polymeric surfactants. Further criteria for classification are for example the subdivision by charge of the hydrophilic part: nonionic (no charged headgroups), anionic (negative charges in the headgroups), cationic (positive charges in the headgroups), or amphoteric (both, positive and negative charges in the headgroups, pH-triggered). A more application-oriented classification is the hydrophilic-lipophilic balance (HLB) concept first introduced by Griffin [54, 55]. The HLB concept classifies the surfactants by balancing the hydrophilic and lipophilic moieties. It is based on a rule established by Bancroft [56, 57], which states that the phase in which the surfactant is soluble to a higher extent forms the continuous phase. Although there are some exceptions, the Bancroft rule is valid for most microemulsions and many macroemulsions [58, 59]. For non-ionic surfactants the HLB can easily be calculated by:
2.2 Multiple emulsions

Figure 2.4: Destabilization mechanisms in W/O/W multiple emulsions. Coalescence controlled mechanisms (top row), diffusion controlled mechanisms (down left and right), and the combined mechanism of swelling-breakdown (right).
2 Background

\[ HLB = 20 \left( \frac{\text{molecular mass of the hydrophilic portion}}{\text{molecular mass of the entire molecule}} \right) \]  

(2.5)

Low HLBs between 3 and 6 indicate W/O emulsifiers, higher HLB numbers from 8 to 13 refer to O/W emulsifiers [59]. Davies [60] introduced refined HLB numbers considering the strength of the hydrophilic and lipophilic groups. A drawback of both HLB concepts is the non-consideration of the temperature influencing the surfactant’s properties. In accordance with the HLB concept, two different surfactants are required to produce multiple emulsions. The first is added to the continuous phase of the inner emulsion, for instance a lipophilic emulsifier for a W/O emulsion. The second has to be of opposite characteristics and is added to the continuous phase in the secondary emulsification step. In case of a W/O/W multiple emulsion a hydrophilic emulsifier would be required for the second step.

In either solute, the surfactant molecule is partly attracted, and partly rejected. This is an adverse situation which the molecules seek to evade by assembly in monolayers at phase boundaries or by self assembly within a phase. If the surfactant concentration exceeds a certain concentration, the so-called 'critical micelle concentration' (CMC) surfactants begin to form aggregates of various structure. Typical self-assembly structures being micelles (in aqueous media) or reverse micelles (in non-polar solvents), bilayer sheets, and vesicles [61–63]. The nature of the aggregate formed depends on the chemical structure and geometry (e.g. cone, truncated cone, cylinder) of the surfactant.

In rotating membrane emulsification it is of importance to employ surfactants with fast adsorption kinetics. In order to reduce coalescence to a minimum, the surface of a droplet forming at the pore outlet has to be covered by surfactant prior to its detachment. Van der Graaf et al. [36] used T-shaped microchannels to investigate the influence of different surfactants on drop formation. For some surfactants no change in resulting droplet size was observable in comparison to the surfactant-free system, indicating an adsorption slower than the drop formation time.

**Laplace pressure.** Interfacial tension causes a capillary pressure difference across a curved interface in a system of two immiscible fluids. This pressure difference, the Laplace pressure \( \Delta p \), is inversely related to the radius of the interface. It can be expressed by the Young–Laplace equation [39, 64]:

\[
\Delta p = \sigma \left( \frac{1}{r_1} + \frac{1}{r_2} \right)
\]

(2.6)
where $r_1$ and $r_2$ denote the radii of the curved interface. For a spherical droplet where $r_1 = r_2$, the Laplace pressure can be described as follows:

$$\Delta p = \frac{2\sigma}{r} \quad (2.7)$$

In the case of two adjacent droplets of different radii, the resulting Laplace pressure inside the smaller droplet is higher. By diffusion through the separating liquid film, the larger droplet grows at the expense of the small one. This phenomenon, known as Ostwald ripening, eventually leads to the disappearance of the small droplet. Laplace pressure also controls the droplet deformation, more energy is needed to deform droplets with small radius and high Laplace pressure [65]. The formation of smaller, more curved droplets, and with this large interfaces, requires a high energy input.

**Osmotic pressure.** The directed flux of molecules across a semi-permeable membrane is referred to as ‘osmosis’. The difference in concentration between the two solutions on both sides of the membrane is to be balanced by a substance able to pass the membrane (often the solvent, e.g. water). The flow takes place in direction towards the solution of higher concentration. In the case of a W/O/W multiple emulsion, the oil layer can be regarded as membrane between the inner W1 droplets and the continuous W2 phase. If the inner aqueous phase is adjusted to a high osmotic pressure, for instance by the addition of an electrolyte, water from the continuous phase is transported through the oil layer into the W1 droplets. Thus, a swelling of the water droplets is caused, which eventually leads to a bursting and the release of entire water droplets including their solutes. This mechanism is also known as ‘swelling-breakdown’ [66]. The osmotic pressure $\Pi$ of a dilute solution can be approximated:

$$\Pi = icRT \quad (2.8)$$

where $c$ stands for the molar concentration of the solution, $R$ for the universal gas constant, $T$ is the temperature. The dimensionless van ’t Hoff factor $i$ is $>1$ if the solute particles dissociate in solution (e.g. $i = 2$ for sodium chloride in water) and $<1$ if they associate in solution. For solute particles neither dissociating nor associating, $i$ equals one.

**Balancing Laplace pressure with osmotic pressure.** The addition of small amounts of electrolytes to the inner water phase can stabilize a W/O/W multiple emulsion. The osmotic gradient induces water transport into the inner droplets, acting as a counterbalance to the outward flow generated by the Laplace pressure. The difference $\Delta P$ between Laplace pressure and osmotic pressure can be
expressed by the following equation derived from Eq. 2.7 and 2.8:

$$\Delta P = \Delta p - \Pi = \frac{2\sigma}{r} - i c_0 \left( \frac{r_0}{r} \right) RT$$

(2.9)

where $c_0$ is the molar concentration of the solution in the original droplet with
radius $r_0$. A high osmotic gradient, caused by a concentrated electrolyte solution
results in a swelling of the droplets and consequently in dilution of the electrolyte
solution leading to a decrease of the osmotic gradient. Due to the swelling and
decrease of the droplet curvature the Laplace pressure also decreases. Accordingly,
too high osmotic gradients leads to droplet bursting including the release of elec-
trolytes to the continuous phase. In this case, the osmotic gradient is decreased
and an pressure equilibrium is reached, but the loss of the inner water droplet is
irreversible. An appropriately chosen osmotic gradient, however, is an excellent
method to achieve stability in multiple emulsions. It is possible to predict the
equilibrium size of a multiple emulsion droplet by equalizing the Laplace equation
with the osmotic pressure difference [49, 67, 68].

Creaming and Sedimentation. The creaming or sedimentation of emulsion
droplets is driven by the density difference $\Delta \rho$ between disperse and continuous
phase. This process affects emulsion stability by bringing the droplets into close
proximity and thus increasing the probability of coalescence. The ascending or
descending velocity $v_s$ of a single droplet is described by Stokes’ law:

$$v_s = \frac{2r^2 \Delta \rho g}{9 \eta_c}$$

(2.10)

A decrease in density difference $\Delta \rho$ or particularly in droplet radius $r$ therefore
leads to reduced creaming velocity, and thus to enhanced emulsion stability. For
very small droplets (micro- or nanoemulsions) the gravitational force is exceeded
by Brownian motion and creaming or sedimentation is prevented [69]. In contrast,
the viscosity of the continuous phase $\eta_c$ has to be increased in order to benefit
emulsion stability. The separation process is driven by the gravitational acceler-
ation $g$, thus emulsion separation is accelerated by strong centripetal forces (e.g.
in a centrifuge). Emulsions with a high $\Delta \rho$ accordingly may be affected by the
centripetal acceleration occurring in a rotating membrane device. However, the
residence time in the head of the device where these forces occur is very short.

In multiple emulsions both, the inner and the outer emulsion may possibly be
affected by creaming and sedimentation. Due to the smallness of the droplets,
these effects are less pronounced in the inner emulsion. The creaming or sedi-
mentation velocity of the larger outer emulsion drops may be decreased by a high
inner emulsion droplet fraction, but only if the presence of these droplets cause the
average density of the outer drops to approach the density of the continuous phase.

**Diffusion.** Assuming the absence of coalescence, the flux \( J \) from regions of high concentration to regions of low concentration across a double emulsion’s oil membrane can be described by Fick’s law \([70]\). According to Fick \([71]\) the flux \( J \) per surface area is proportional to the concentration gradient \( dc/dx \):

\[
J = -AD \frac{dc}{dx} \quad (2.11)
\]

with \( A \) being the area across which the diffusion occurs. The minus sign in the equation is due to the fact that the direction of the diffusion is opposed to the concentration gradient. Fick’s first law also includes a proportionality constant \( D \), the diffusion coefficient. For the diffusion of spherical particles through liquids with low Reynolds number, the diffusion coefficient \( D \) is described by the Stokes-Einstein equation:

\[
D = \frac{k_B T}{6 \pi \eta r} \quad (2.12)
\]

where \( k_B \) is the Boltzmann’s constant, and \( \eta \) the viscosity of the liquid. \( T \) stands for the absolute temperature and \( r \) for the radius of the particle. The diffusion flux therefore mainly depends on the magnitude of the concentration gradient, but is also influenced by further factors such as the temperature, the size of the diffusing particle, and the viscosity of the surrounding medium.

Fick’s second law is concerned with non-steady-state diffusion. It describes the change of concentration with respect to time:

\[
\frac{dc}{dt} = D \frac{d^2c}{dx^2} \quad (2.13)
\]

### 2.2.2 Release mechanisms

Release of water and water soluble materials enclosed in the inner W1 water phase occurs by two main pathways: i) coalescence between inner water droplets and the continuous water phase, and ii) lipophilic surfactant assisted permeation through the intact oil film separating the two aqueous phases. A combined mechanism, the so called ‘swelling-breakdown’ leads to potential acceleration of the release. Thereby, an osmotic gradient is adjusted by the addition of electrolytes to the inner water phase. Water diffuses through the oil layer leading to a swelling and to an eventual bursting of the inner droplets, thereby releasing the enclosed drug or marker substance.
Several mechanisms are suggested in literature for the surfactant assisted permeation of ionized and nonionized water-soluble materials through the lipophilic phase.

- A frequently mentioned mechanism is the inclusion and transport of water and water soluble substances into reverse micelles formed in the oil phase by the lipophilic surfactant [8, 72–76].

- Kita et al. [72] additionally proposed the passage through thin surfactant lamellae in the oil layer formed due to local changes of the oil layer thickness. This mechanism later was termed "thermally activated holes“ [77, 78] and according to Hamilton and Kaler [79] such transient pores occur in vesicle bilayers. Hamilton also claims, that the transient pores are lined with surfactant monomers, and that ion transport through these holes only takes place for very thin bilayers with a maximum diameter of 30 Å.

- The third mechanism, proposed by Colinart et al. [8], is the transportation of water molecules via hydrated surfactant molecules.

The transport mechanisms are schematically depicted in Fig. 2.5. Some authors [80–82] also reported the observation of a spontaneous emulsion droplet formation in the lipophilic phase. Spontaneous emulsification is the formation of emulsion droplets without input of agitation energy required when the two immiscible phases are brought into contact [83]. Several possible mechanisms are proposed to explain the spontaneous formation of emulsions including interfacial turbulence, negative interfacial tension, and diffusion and stranding [84]. The formation of thermodynamically stable microemulsions depends on many parameters such as temperature, surfactant [85] and electrolyte content [86]. The question to which extent the spontaneous emulsification contributes to the transport of water and entrapped substances is not yet solved conclusively.

### 2.2.3 Parameters influencing release

Water transport through the oil membrane is driven by the osmotic pressure gradient and Laplace pressure. Even the addition of equimolar concentrations of two different sugars to the two aqueous phases possibly leads to an osmotic gradient. In that case the occurrence of the gradient was depending on the difference in number of equatorial-OH groups in the sugars [87]. Furthermore, the transport is influenced by various parameters:

- *Oil film thickness* was found to have an influence on the transport rate. Wen and Papadopoulos [74, 81] claimed that the distance between the two aqueous phases determines the transport mechanism: water transport rates...
between two droplets visually in contact were found to be about a factor 20 higher than between two non-contacting droplets. Additionally, for the

Figure 2.5: Water transport through a thin oil film a) via reverse micelles, b) by passage through thin lamella of surfactant, c) by hydrated surfactants. •— lipophilic surfactant, ◦— hydrophilic surfactant.

non-contacting droplets, the spontaneous formation of emulsion droplets was observed. The conclusion was drawn, that for thicker oil films reverse micellation and spontaneous emulsification are responsible for the transport, for very thin films however, the hydrated surfactant mechanism is controlling the transport.

• Pays et al. [48] observed that the amount of hydrophilic surfactant influences the double emulsion stability. Release of encapsulated matter occurred very
fast and mainly due to W1-W2 coalescence, when the hydrophilic surfactant was added in amounts \( > \text{CMC} \). Wen and Papadopoulos [80] found faster film rupture with increasing hydrophilic surfactant concentration in W2.

- The importance of the *lipophilic surfactant* was discussed in many publications. Most authors agree that an increase in lipophilic surfactant acting as carrier favors water transport [46, 73, 88–90], in particular for very thin oil layers [80]. Nevertheless, Colinart et al. [8] and Matsumoto et al. [91] observed a decrease in transport rate if a certain surfactant concentration was exceeded. This decrease was explained by the increasing oil film viscosity [8, 73], supported by Bonnet et al. [78] who reported an increasing marker transport with decreasing oil phase viscosity.

- *Electrolyte presence* not only has an influence on the osmotic gradient but also on the *interfacial layers* [1]. The electrolyte might compete for water molecules against the surfactant at the oil-water-interface resulting in a rigid interfacial film and hindering the transfer of water and drug [7].

- Viscosity and elasticity [92] of the W1/O and O/W2 interfaces are important for the stability of the emulsion, e.g. by preventing coalescence or inhibiting contact between two droplets. The *nature of the oil layer* also influences the release of a marker substance. In addition to the influence of the viscosity, Bonnet et al. [78] found a correlation between the number of saturated fatty acids, and the release of the enclosed electrolyte.

- Omotosho et al. [90] also investigated the influence of the oil phase nature, but correlated the difference in transport rate with the differed *droplet size*. Droplet size influences the release by determining the interfacial area available for mass transfer.

- Another important factor is the increase in *temperature* leading to a decrease in viscosity, potentially changing the solid fat content of the oil layer [93], and accelerating diffusion [76].

### 2.2.4 Marker transport

Contradictory observations regarding the transport of electrolytes and marker substances have been reported. To distinguish release due to swelling-breakdown from release due to permeation through the oil phase is rather difficult in multiple emulsion systems. Jager-Lezer et al. [46] suggested swelling-breakdown to be the only way to release the hydrophilic marker substance, hydrated magnesium sulfate, and Raynal et al. [94] also reported the absence of diffusion for the same compound. Magdassi and Garti [95] on the contrary, claimed that the migration
of sodium chloride was primarily controlled by diffusion. Cheng et al. [75] were investigating the transport of ions through the oil phase in a two-droplet model system and could confirm ion transport devoid of breakdown. Due to the fact that significantly less ion transfer occurred, when the droplets were visually contacting, the authors concluded reverse micellation to be the mechanism for ion transport. For visually non-contacting droplets the transport rate was independent from the membrane thickness in the investigated range (30 – 120 µm). Ions with small Pauling radius were easier entrapped in reverse micelles, and therefore transported faster.

2.3 Rheology of emulsions

Rheology is the study of deformation and flow of matter [96]. It includes the flow behavior of fluids as well as the deformation behavior of solids. For most rheological tests, a well-defined force is applied to a material and the resulting deformation or flow is observed. In emulsion science, rheology is a widely-used method to gain insights on emulsion stability, structure, and on interactions between different components of the system [97, 98].

Shear rheology is the shearing of a sample in a gap between two walls, one of which is moving. The simplest way to perform shear rheology is rotational rheometry. This method uses steady shear either with controlled shear rate $\dot{\gamma}$ (CSR mode) or with controlled shear stress $\tau$ (CSS mode). In oscillatory rheology, the direction of the shear oscillates sinusoidal in short intervals. Frequency $f$ and deformation $\gamma$ are the parameters determining the oscillation.

2.3.1 Factors influencing emulsion rheology

An emulsion’s properties, such as droplet rigidity, volume fraction of the dispersed phase, or droplet size strongly influence its rheology. The main parameters are covered below.

Disperse phase fraction. An emulsion’s viscosity strongly depends on the disperse phase fraction $\phi$. For dilute emulsions of low disperse phase fraction $\phi \leq 0.01$ the relative viscosity $\eta_r$ may be calculated using the simple Einstein equation [99]:

$$\eta_r = 1 + k_1 \phi$$  \hspace{1cm} (2.14)

where the relative viscosity $\eta_r$ is defined as the ratio of the emulsion’s viscosity $\eta$ to the viscosity $\eta_c$ of its continuous phase. As soon as the disperse phase fraction
2 Background

exceeds the Einstein limit of $\phi = 0.01$, Brownian motion and hydrodynamic interaction have to be taken into account. Batchelor [100] proposed an expansion of the Einstein equation (Eq. 2.14) for more concentrated emulsions ($0.01 \leq \phi \leq 0.2$):

$$\eta_r = 1 + k_1 \phi + k_2 \phi^2$$

(2.15)

where $k_1$ is Einstein’s coefficient (equal to 2.5 for rigid spheres) and $k_2$ (equal to 6.2) accounts for hydrodynamic two-body interaction [100].

For still higher volume fractions of $\phi \geq 0.2$, the emulsion’s relative viscosity becomes a complex function of its volume fraction. A semi-empirical equation relating the relative viscosity of a concentrated emulsions to the intrinsic viscosity $[\eta]$ and the maximum packing fraction $\phi_{\text{max}}$ is given by Krieger and Dougherty [101]:

$$\eta_r = \left(1 - \frac{\phi}{\phi_{\text{p}}}ight)^{-[\eta] \phi_{\text{p}}}$$

(2.16)

Another approach considering rheology of concentrated emulsions focuses on the expansion of Eq. 2.15 with a fourth term $k_3 \phi^3$. According to Tadros [69] only semi-empirical solution approaches for $k_3$ can be found in literature.

**Rigidity of the droplets.** The rheological behavior of very rigid droplets, for instance highly viscous oil droplets suspended in an aqueous phase of low viscosity, is comparable to the one of suspensions. Therefore the challenges known in suspension rheology, for example apparent wall slip or aggregation, are relevant for emulsion rheology too. Emulsions containing deformable droplets exhibit different relative viscosities $\eta_r$ compared to suspensions. Especially for medium to high shear rates the relative viscosity is reduced due to drop deformation and orientation. However, for very high shear a viscosity increase over time (rheopexy) may occur due to drop disruption. [102]

Due to the flow field of the surrounding continuous phase, the liquid within a fluid droplet is caused to circulate. This implies less energy dissipation due to friction, and thus a lower relative viscosity than predicted by the Einstein equation (Eq. 2.14) [97]. Taylor [103] proposed an expansion to Einstein’s suspension theory for deformable droplets:

$$\eta_r = 1 + \left(\frac{\eta_c + 2.5 \eta_d}{\eta_c + \eta_d}\right) \phi$$

(2.17)

For emulsions containing highly viscous droplets ($\eta_d \gg \eta_c$) this equation tends towards the Einstein equation for rigid spheres. For emulsion systems with a
low dispersed phase viscosity \( \eta_d \ll \eta_c \), e.g. foams) the equation 2.17 tends to 
\[ \eta_r = 1 + \phi \] [97].

**Droplet size distribution.** According to Pal [104] the droplet size strongly affects the viscosity of concentrated emulsions. Emulsions of small droplet size exhibit considerably higher viscosities as well as more pronounced shear-thinning. Regarding an emulsion’s resulting viscosity the polydispersity of the system was found to be of even more importance than the droplet size. Furthermore an emulsion’s maximum packaging fraction \( \phi_{max} \) can reach higher values as a result of polydispersity. The viscosity of a monodisperse emulsion with a disperse phase fraction of \( \phi = 0.4 \) was found to be three times the viscosity of a very polydisperse emulsion of identical disperse phase fraction [104, 105].

### 2.3.2 Rheology of multiple emulsions

Rheology is often used to investigate the stability and internal microstructure [97] of multiple emulsions, to monitor release kinetics, swelling, and/or breakdown [52, 94, 106–109]. Nevertheless, only very few publications deal with the theoretical aspects of multiple emulsion rheology [110–112], claiming that no other model but the two step approach presented by Pal [112] is available for the description of rheological response functions of multiple emulsions containing many inner droplets.

### 2.3.3 Rotational rheology of concentrated multiple emulsions

**Yield stress.** Highly structured, concentrated emulsions dominated by droplet interaction are known to display yield stress characteristics. However, not only the definition of the term ‘yield stress’ causes controversy but some authors even questioned the existence of such, acknowledging yield stress to be a useful approximation only [113]. A detailed discussion of this subject can be found elsewhere [114–116]. In this thesis, yield stress is defined as the minimum stress required to enable flow caused by a breakdown in the structure of the multiple emulsion. A shear stress lower than this yield stress only causes elastic deformation. Fig. 2.6 displays a typical flow curve of a concentrated emulsion showing an upper zero viscosity plateau at low shear stresses, a sudden viscosity decrease over several orders of magnitude in a narrow range of shear stress, indicating an apparent yield
stress \(\tau_c\), and a low viscosity power-law region at high shear stresses.

**Vane rheometry.** The vane geometry is an often used method to measure yield stresses in systems displaying strong wall slip effects at smooth walls \[117\]. This geometry’s thin blades can be introduced into such systems with least destruction possible to the structure of the sample. It is assumed that the fluid ruptures or yields along a cylindrical surface, therefore the vane geometry is considered to be a concentric cylinder with a diameter equal to the blade length \[118\]. The absence of secondary flow between the blades is a precondition for reliable measurements. This assumption allows the transformation of rheometer torque \(T\) into shear stress \(\tau\) as follows \[119–122\]:

\[
\tau = \frac{2T}{\pi D^3 \left( \frac{H}{D} + \frac{1}{3} \right)}
\]

(2.18)

with \(D\) being the diameter and \(H\) the height of the geometry. If the infinite gap approximation is made, the shear rate \(\dot{\gamma}\) can be derived from the angular velocity \(\Omega\) and the power-law index \(n\) for the corresponding fluid \[117, 121, 123\]:

\[
\dot{\gamma} = \frac{2\Omega}{n}
\]

(2.19)

For Newtonian fluids, the power-law index \(n\) equals 1. The power-law index for non-Newtonian fluids displaying yield stress characteristics can be determined by plotting torque \(T\) against the angular velocity \(\Omega\) in the power-law region and calculating the value of \(d(\ln T)/d(\ln \Omega)\) (the power law region can be seen in Fig. 2.6). The infinite gap approximation can be made due to the insertion of the vane geometry into a large cup of sample. Further advantages the use of the vane geometry in large beakers offers are the avoidance of wall slip effects and the reduction of sample damage during loading \[121\].

**Composite Ellis model.** The flow curves obtained in the case of concentrated emulsions or multiple emulsions can be fitted using a composite Ellis model as suggested by Roberts et al. \[124\]. This model is suitable for materials displaying a "sharp precipitous fall-off from a high-viscosity Newtonian plateau, then a second, more gradual fall, but with no obvious high-shear-stress asymptote within the range of the data available" \[124\]. The composite Ellis model, shown in Eq. 2.20 to 2.22, consists of the Ellis model \[125\] (Eq. 2.20) with redefined parameters zero viscosity \(\eta_0\) and infinite viscosity \(\eta_\infty\). In the composite Ellis model these previously constant parameters become functions \(\eta_0'\) and \(\eta_\infty'\) of the shear stress \(\tau\) (Eq. 2.21, 2.22).
2.3 Rheology of emulsions

![Flow curve of a concentrated double emulsion](image)

Figure 2.6: Flow curve of a concentrated double emulsion measured by vane geometry showing upper zero viscosity plateau, yield stress region, and power-law region.

\[
\frac{\eta - \eta'_{\infty}}{\eta'_0 - \eta'_{\infty}} = \frac{1}{1 + (\tau/\tau_c)^m} \tag{2.20}
\]

where

\[
\eta'_0 = \eta_0 \left( 1 + (\tau/\tau_1)^p \right) \tag{2.21}
\]

and

\[
\eta'_{\infty} = \eta_{\infty} \left( 1 + (\tau/\tau_2)^s \right) \tag{2.22}
\]

The critical stress \(\tau_c\) is denoted as the fitted yield stress, \(\tau_1, \tau_2, m, p\) and \(s\) are fitted parameters. The parameter \(s\) is negative, in order to allow \(\eta'_{\infty}\) to level off at high stresses after displaying power-law characteristics at lower stresses.

2.3.4 Oscillatory rheology of concentrated multiple emulsions

Oscillational rheology measures the phase shift \(\delta\) between an applied sinusoidal stress \(\tau(t)\), and the resulting sinusoidal strain \(\gamma(t)\) (or vice versa). According to Hooke’s law the complex shear modulus \(G^*\) can be calculated:

\[
\text{23}
\]
The storage modulus $G' = (\tau_A/\gamma_A) \cos \delta$ represents the elastic behavior of the sample, and the loss modulus $G'' = (\tau_A/\gamma_A) \sin \delta$ stands for the viscous behavior of the sample, for $\gamma_A$ being the amplitude of $\gamma(t)$, and $\tau_A$ being the amplitude of $\tau(t)$.

The loss factor $\tan \delta = G''/G'$ gives information about the ratio between viscous and elastic behavior. For ideal elastic behavior the loss factor $\tan \delta = 0$, for ideal viscous behavior, $\tan \delta = \infty$. If the viscous and the elastic behavior of a sample are equal (i.e. $G' = G''$) the loss factor becomes $\tan \delta = 1$.

Oscillational rheology is an useful method to investigate the changes in a sample over time without destroying its structure. The sample is sheared at constant frequency and amplitude, $G'$ and $G''$ are recorded. For this approach it is important to choose deformations for which the sample structures are not changed or destroyed. Hence, the impact of increasing deformation has to be analyzed in an amplitude sweep test. This test increases the amplitude at constant frequency, and thus determines the linear viscoelastic (LVE) range. $G'$ and $G''$ are plotted...
as a function of stress or strain, as shown in Fig. 2.7. In the LVE range, $G'$ and $G''$ show constant values. If the amplitude exceeds a critical value $\gamma_L$, both moduli drop and the sample structure is changed. In the case of multiple emulsions such an irreversible change denotes drop breakup, coalescence, or release of inner aqueous phase. Therefore it is essential to perform all oscillatory measurements strictly in the linear viscoelastic range.

### 2.4 Polyglycerol polyricinoleate (PGPR)

In this work the primary focus is on the effect of non-ionic surfactant polyglycerol polyricinoleate on multiple emulsion stability and transport phenomena through lipid layers. Therefore, the production process, physical and chemical properties, applications, as well as possible health hazards of PGPR are reviewed in detail in the following chapter.

Figure 2.8: Structure of polyrinoleic acid, polyglycerol, and principal structure of PGPR. At least one group marked R is a polyricinoleic acid, the other ones may be hydrogens, fatty acids, or polyricinoleic acids [126–128].

#### 2.4.1 Production

Polyglycerol polyricinoleate, as the name implies, is mainly composed of ricinoleic acids and glycerol. Its chemical structure in general form is shown in Fig. 2.8.
PGPR is prepared in a four-stage process: (i) preparation of the castor oil fatty acids by hydrolising castor oil, (ii) fatty acid condensation until there are no more than five fatty acid residues per molecule of the condensed product remaining, (iii) condensation of two or more molecules of glycerol to polyglycerol with subsequent removal of the unchanged glycerol, and (iv) finally the esterification of the polyricinoleic acids to the polyglycerol headgroup. The condensation in step (ii) and (iv) is carried out under vacuum at elevated temperatures, under addition of carbon dioxide in order to prevent oxidation. The preparation of the polyglycerol (iii) is carried out under alkaline conditions at high temperatures, again in the presence of carbon dioxide [129].

Since PGPR is produced rather from condensed castor oil than from pure ricinoleic acid, other fatty acids can be found in the product as well. According to Wilson et al. [129], castor oil contains 80–90 % of ricinoleic acid, 3–8 % of oleic acid, 3–7 % of linoleic acid, and 0–2 % of stearic acid. If instead of ricinoleic acid an other fatty acid, e.g. oleic acid, is linked to a polyricinoleic acid, it acts as a chain terminator. The polyglycerols are only partly esterified. The free hydroxyl-groups, together with the hydroxyl-groups of terminal ricinoleic acids, represent the hydrophilic parts of the product. Furthermore, the reaction mixture contains free fatty acids and polyglycerins [128].

### 2.4.2 Physicochemical properties

PGPR is a clear, brown, or yellow liquid, which is viscous at ambient temperature. Under thermal impact migration of the acyl groups may occur. Nevertheless the thermal stability is good, no adverse effects were detected after 14 days storage of PGPR samples at 60°C. Due to the large lipophilic part no formation of mesomorphic phases is expected [128, 130]. According to Adams and Schuster [128], PGPR is insoluble in cold and hot water, dispersible in ethanol or glycerol, and soluble in isopropanol and lipophilic substances. Specifications for the HLB of PGPR found in literature differ from "moderately low“ [131] to "low“ [93] to ”< 1“ [132].

### 2.4.3 Fields of application

Of the wide range of emulsifiers used in foods, polyglycerol polyricinoleate is one of the most hydrophobic [133] and gives one of the most powerful water-in-oil emulsifiers [134]. In the food industry PGPR is mainly used in block chocolate
and chocolate couverture but it is also used as an emulsifier for tin-greasing [129].
PGPR addition leads to a strong decrease in yield stress of melted chocolate
whereas viscosity is only slightly lowered. The yield stress decrease caused by
PGPR is much more pronounced than the one caused by lecithin, however best
results are achieved by combining both emulsifiers [135]. The application of such
lecithin-PGPR blends allows to adjust the flow properties of molten chocolate,
confectionery coatings, and fat-based fillings [136]. The reduced yield stress results
in better moulding due to increased release of entrapped air, which leads to thinner
and more uniform coatings [135]. Due to its excellent water binding properties
[133] PGPR is also used in coatings for ice-cream. It is able to reduce viscosity in
the presence of small quantities of water, which otherwise would lead to thickening
of the coating [129].

2.4.4 Legislation and safety

According to the Swiss food additives ordinance, PGPR (food additive E476) is
only approved for limited applications: It can be used in amounts up to 4 g/kg
for the production of margarine, low fat spreads, mayonnaise, and dressings, in
amounts up to 5 g/kg for chocolate and cocoa products [137]. According to EU
regulations [138] the polyglycerol moiety has to consist of at least 75% of di-, tri,
and tetracylglycerols and of no more than 10% of polyglycerols equal or longer than
heptacylglycerol.

PGPR proved to be degradable in rats intestine to a mixture of polyglycerols
and polyricinoleates, which was not detectable in tissue samples indicating either
no adsorption, or an efficient metabolization to water and CO$_2$ [139]. Neither ad-
verse effects on rat growth and reproductive capacity [140] nor any carcinogenic
potential was observed [141]. In human studies was demonstrated that the lipid
metabolism is not affected by PGPR. Wilson and Smith [142] concluded there are
no adverse effects of PGPR consumption on human health.
3 Multiple emulsions prepared by rotating membrane emulsification

3.1 Introduction

Multiple emulsions may also be termed as emulsions of emulsions. Generally, they are produced in a two step process; first a simple emulsion is made, then the inner emulsion is dispersed into an outer continuous phase. Due to their potential for encapsulation and release of substances, multiple emulsions have promising applications in food, cosmetic, and pharmaceutical industries, as well as in separation processes [1, 2].

In conventional turbulence based emulsification processes such as rotor/stator devices or high-pressure homogenizers, high shear forces are applied to disrupt droplets in order to achieve emulsions with small average droplet diameters [3]. Consequentially, the very high volumetric energy input possibly causes the destruction of shear or temperature sensitive ingredients, such as proteins. Due to the repeated droplet rupturing, considerable amounts of inner phase might leak into the continuous phase, resulting in a substantial loss of encapsulated substance. Therefore, conventional methods are only suitable to a limited extent to produce multiple emulsions.

It is known that the membrane emulsification technique is a suitable method to produce multiple emulsions as only mild stresses are applied to the system [2]. Cross-flow membrane emulsification, however, is not very suitable for industrial applications due to the dependency between droplet size and flow rate and the thus resulting need of recirculation. Schadler and Windhab [4] introduced a rotating membrane device in pilot-plant scale that enables a variation in droplet size by adjusting the rotational speed of the cylindrical membrane. The setup allows the production of emulsions with high dispersed phase fractions without recirculation. In this chapter, the advantages of the ROME device are investigated for the production of multiple emulsions at pilot-plant scale (10 - 2001/h, depending on the phase ratio).
Multiple emulsion systems are thermodynamically unstable, usually a large part of the internal phase is lost during production or storage. For certain applications, however, such as drug delivery, this instability might be desired in order to achieve a controlled release of encapsulated substances [5, 6, 44]. In this thesis, multiple emulsions of W/O/W type with electrolytes enclosed in the inner aqueous phase are produced by rotating membrane device. The electrolyte leads to a swelling-breakdown process where the continuous aqueous phase diffuses through the oil phase and causes a swelling of the inner water droplets. Due to the swelling and the depletion of the continuous phase, a multiple emulation of medium to very high viscosity containing a high proportion of enclosed water is produced. With a satisfying long term stability such a system is of considerable interest in cosmetics or food industries. In this work the influence of important parameters, such as surfactant or electrolyte, on the swelling-breakdown, the rheological properties, and on the stability of the multiple emulsion system are investigated.

Nomenclature. In multiple emulsions, the phases are determined by the order of mention i.e. from inside to outside. In a W1/O/W2 emulsions, W1 represents the innermost, O the intermediary, and W2 the outermost phase. Phase ratios are described in a similar manner. The ratio of the inner emulsion is listed in brackets, followed by the phase ratio of the outer emulsion, for example (20/80)-50/50. The inner W1/O emulsion, the 'primary emulsion', is produced in the 'primary emulsification step'. Correspondingly, the outer, multiple W1/O/W2 emulsion, the 'secondary emulsion', is produced in a 'secondary emulsification step' where the primary emulsion is mixed into an outer continuous phase.

3.2 Experimental

3.2.1 Materials

Aqueous phases. Deionized water was used for both aqueous phases and for dilution of the sample for further analysis. The hydrophilic surfactant polyethylene glycol sorbitan monolaurate, (Tween 20, Sigma Aldrich, Switzerland), was mixed into the outer aqueous phase in a concentration of 2 wt%. The non-ionic detergent mainly used for emulsions of O/W type has a HLB-value of 16.7±1.0 and is available as high-viscous liquid. As electrolyte, common table salt (JuraSel Speisesalz, Schweizer Rheinsalinen, Switzerland) was used. According to the product specifications, JuraSel consists of at least 99.8% sodium chloride. Emulsions made of the ingredients listed above are referred to as 'standard system'.
3.2 Experimental

Experiments were performed using a model food system. Commercial spirit vinegar (Spreewald-Konserven-Feldmann GmbH & Co, Germany) containing 11% acid was used for microbiological stabilization. It was added to both, inner and outer aqueous phase in a concentration of 10 wt% to avoid a pH gradient. Furthermore, the emulsifier Tween 20 was replaced by spray dried pasteurized egg yolk powder (AMP Altland Eierprodukte, Germany). The powder was reconstituted by water added in a ratio of 1:1.25. The reconstituted egg yolk was added to the outer aqueous phase in concentration of 35 wt%. For additional stabilization of the emulsion, 10 wt% of mustard (Thomy, Nestlé Suisse S.A., Switzerland) was also added to the outer aqueous phase.

**Oil phase.** Commercially available sunflower oil (Florin AG, Switzerland), extracted from sunflower seeds, was used without additional purification. Sunflower oil (SFO) is a natural product with high variations in its composition and containing impurities. It consists of triglycerides, a small amount of diglycerides plus some free fatty acids which may exhibit surface activity. Tab. 3.1 lists the average content of fatty acids in Florin SFO determined by gas-liquid chromatographic method [143]. As a lipophilic emulsifier, Grindsted PGPR 90 (Danisco AG, Denmark) was used as received. PGPR is produced from condensed castor oil, therefore it also contains other fatty acids than rinoleic acids. All fatty acids are either esterified to a PGPR molecule, or can be found as free fatty acids in the mixture. Furthermore, unesterified polyglycerins can be found in the product. The molecular structure of PGPR is depicted in Fig. 2.8.

<table>
<thead>
<tr>
<th>Fatty Acid</th>
<th>Content [%]</th>
<th>Fatty Acid</th>
<th>Content [%]</th>
</tr>
</thead>
<tbody>
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<td>0.07</td>
</tr>
<tr>
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<td>elaidic C18:1 trans</td>
<td>0.06</td>
</tr>
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<td>oleic C18:1 cis</td>
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</tr>
<tr>
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<td>gondoic C20:1 n-9</td>
<td>0.18</td>
</tr>
<tr>
<td>behenic C22:0</td>
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<td>C18:2 trans</td>
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</tr>
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<td>linoleic C18:2 n-6</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>C18:3 trans</td>
<td>0.03</td>
</tr>
<tr>
<td>α-linoleic C18:3</td>
<td></td>
<td>n-3</td>
<td>0.26</td>
</tr>
</tbody>
</table>
3 Multiple emulsions prepared by rotating membrane emulsification

3.2.2 ROME

**Rotating membrane device.** A continuously working rotating membrane device (FM 1-56 SO, Kinematica AG, Switzerland) consisting of an emulsification head, a motor, and a frequency inverter was utilized. The emulsification step took place in the head of the device (Fig. 3.2). The head is composed of a cylindrical membrane module, mounted concentrically onto a hollow shaft, and an outer cylinder, which is also mounted concentrically (Fig. 3.1). The inner diameter of this second cylinder can be varied in order to adjust the shear gap width. The membrane modules had a diameter of 56 mm and a length of 60 mm. The gap width between membrane surface and cylinder wall was set to 1 mm. The dispersed phase (in the case of multiple emulsions the inner W1/O emulsion) was pumped through the hollow shaft into the membrane module and was forced through the pores of the module. The continuous phase flowed through the gap between membrane module and outer cylinder.

![Fig. 3.1: Assembly of the ROME head. A sintered wire mesh membrane fixed on the hollow shaft (A), and with mounted outer cylinder determining the shear gap of 1 mm (B).](image)

**Membranes.** Two types of membranes are available for membrane emulsification. Unless otherwise noted, a Poremet mesh membrane (Bopp AG, Switzerland) was used in our experiments. This metal sheet-like laminated construction consists of five different layers made of woven wire mesh sintered together. Two of these layers act as support tissue, one as drainage tissue, and one as protective layer. The most close-meshed layer has a nominal pore size of 2 μm and determines the size of the emerging droplets. Due to the less defined shape of the pores and the small distance between pores, the mesh membrane is considered to lead to more coalescence and to a wider droplet size distribution than the so-called controlled pore
3.2 Experimental

distance (CPDN) membrane. The CPDN membrane represents an almost ideal configuration with uniform pores and well-defined large spaces between pores. It theoretically allows the generation of uniform droplets and the prevention of coalescence during droplet formation on the membrane surface. It was purpose-built for the rotating membrane emulsification process [26]. A flat photo-etched nickel based microsieve (Stork Veco B.V., Netherlands) was coated to reduce the pore size while maintaining the pore uniformity and shape. The carbon coating resulted from a plasma assisted chemical vapor deposition (PACVD) process [144] and led to a reduction of the pore diameter from 5 µm to 1.5 µm. Even though the CPDN membrane is a promising tool to produce emulsions with the rotating membrane device, it still shows unsolved stability problems concerning the fixation of the membrane sheet on a cylindrical membrane module. Therefore, in this work we mostly employed the mesh membrane for emulsion production.

![Schematic drawing of the ROME head.](image)

Figure 3.2: Schematic drawing of the ROME head.

3.2.3 Experimental setup

Additionally to the rotating membrane device, two pumps were part of the experimental setup. The continuous phase was conveyed by an eccentric worm pump (Nemo NM008BY03512b, Häny AG, Switzerland), the disperse phase by a gear pump (MCP-Z, Ismatec SA, Switzerland). The pressure of the dispersed phase on the membrane was measured at the phase inlet. Temperature was controlled at the dispersed phase inlet and at the final product outlet. The flow rates of both phases were monitored using two oval wheel counters (B.I.O-TECH e.K., Germany), which were calibrated for every experiment. The flow sheet of the
Multiple emulsions prepared by rotating membrane emulsification

emulsification process is shown in Fig. 3.3. To the outer cylinder of the emulsification chamber a cooling jacket can be mounted. In order to maintain the droplet detachment mechanism for all different phase ratios (dispersed to continuous phase), the continuous phase flow-rate was adjusted only. The flow rate of the disperse phase was kept at 150 ml/min for the standard system, and at 100 ml/min for the model food system, respectively.

![Figure 3.3: ROME process flow sheet.](image)

3.2.4 Rotor/stator emulsification

The rotor/stator device Megatron MT 5000 (Kinematica AG, Switzerland) was used for comparative production test. The continuously working system consists of a motor, a frequency converter, and an emulsification chamber. Various dispersing geometries can be interchanged. In this thesis the MTG 36/4 generator was used, a rotor/stator geometry with two rows of teeth each and with diameters of 30 mm (rotor) and 36 mm (stator) respectively. The rotating speed can be varied from 5000 rpm up to 20 000 rpm. The experimental setup was similar to the rotating membrane setup including two pumps, temperature control, and monitoring of the flow rates.
3.2 Experimental

3.2.5 Production of the W1/O emulsion

The dispersed inner emulsions were produced batchwise by the rotor/stator device Polytron PT6000 (Kinematica AG, Switzerland) using the PTG 40/2 dispersing aggregate. SFO and lipophilic emulsifier were mixed at low rotational speed. In a pre-emulsification step the aqueous phase was added slowly during 4 min at a stirring speed of 4000 rpm. After the appropriate amount of water (20 to 50 wt\%) was dispersed into the oil phase, the main emulsification step was carried out at 8000 rpm in order to reduce the droplet size further. Stirring times as well as the batch size were maintained within a series of experiments.

3.2.6 Rheology

All rheological measurements were performed using a MRC 300 rheometer (Anton Paar GmbH, Austria) equipped with a circulating water bath and a peltier temperature control system (TEZ 150 P/MCR). A couette concentric cylinder cell (CC27) and a double-gap couette cell (DG26.7) were used to determine flow curves as well as for oscillatory time sweeps. In order to determine the linear viscoelastic range, strain sweeps ($\gamma = 0.1 - 100$ \%) and frequency sweeps ($f = 0.5 - 100$ Hz) of several samples were investigated. The parameters for the oscillatory time tests were set to $\gamma = 0.5 \%$, $f = 3$ Hz for the standard system and to $\gamma = 1 \%$, $f = 3$ Hz for the model food system. All experiments were performed at 20°C.

Furthermore, a four blade vane geometry (diameter 22 mm, blade length 22 mm) was used without temperature control. The vane geometry was utilized to determine yield stresses of highly viscous model food system samples inside the storage beakers directly. In order to achieve similar immersion depths of the vane geometry, all storage cups were filled to the same height approximately. The shear stress was then increased logarithmically every 8 sec starting at 10 Pa. The measurement was stopped after the lower infinite viscosity plateau was reached.

Shear stress $\tau$, shear rate $\dot{\gamma}$, and apparent viscosity $\eta$ were calculated using Eq. 2.18 and 2.19, assuming a Newtonian fluid ($n = 1$ in Eq. 2.19). The simplification was possible because the experiments were of comparative nature only. The inclusion of the non-Newtonian index would solely influence the absolute viscosity (y-axis direction in Fig. 2.6) but not the yield stress (x-axis direction in Fig. 2.6), which was actually of major interest in this work. The calculated viscosities are no ab-
solute values and are therefore called apparent viscosities. The data were fitted using the composite Ellis model (Eq. 2.20 to 2.22) to determine yield stress $\tau_c$.

### 3.2.7 Laser diffraction particle size analysis

Laser diffraction particle size analysis was used to characterize the inner water droplets before the second emulsification step, as well as double emulsion oil droplets in the outer water phase. Particle size distribution was determined using a Beckman Coulter LS 13320 (Beckman Coulter Inc., USA). The Coulter LS 13320 allows the determination of droplet diameters between 0.04 and 2000 $\mu$m. Two sample handling modules (universal liquid modules, ULM) with different carrier liquids (sunflower oil and deionized water) were available for the two different emulsion types (W/O and O/W). Every sample was measured three times. Highly viscous or optically very dense samples had to be diluted with the corresponding carrier liquid prior to the injection. Sample was injected until an obscuration level of 8 to 12 % was achieved. The inner W1/O emulsions were measured using Mie theory and refractive indices of 1.332 for water and 1.45 for SFO. The size of multiple emulsion droplets was determined using the Fraunhofer theory.

### 3.2.8 Microscopy

**Light microscopy** enabled a visual estimation of multiple emulsion droplet sizes, oil droplet filling degree, and emulsion stability. The inverted light microscope Leica CM IRB (Leica Microsystems GmbH, Germany) was utilized to acquire pictures by a CCD-camera. Due to their high optical density, the samples had to be diluted with deionized water beforehand.

**Confocal laser scanning microscopy** (CLSM) allowed a visualization of the multiple emulsion sample without dilution. A Leica SP1-2 confocal laser scanning microscope (Leica Microsystems GmbH, Germany) with a Ar/Kr laser was used. The fluorescing agent Nile red (Sigma Aldrich, Switzerland) with excitation wavelength at 488 nm and emission maximum at 518 nm was utilized as an oil soluble fluorescing agent. The focus point of the laser was set to a point inside the emulsion sample.
3.3 Double emulsion preparation by rotating membrane

The rotating membrane device was employed to combine the possibility of a narrow droplet size distribution and the gentleness known from cross-flow membrane emulsification [23], with the advantages of conventional emulsification processes. This includes droplet detaching forces independent from the velocity of the continuous phase, and hence no dependency of the resulting droplet size on the phase ratio. Especially the rotating CPDN membrane with its uniform pores was expected to produce monodisperse emulsions [26], but these expectation was not fully met. Bimodal distributions were frequently found, a fact which was attributed to the generation of secondary drops (i.e. satellite droplets) formed during drop detachment at the pores [37]. In the course of the experiments, however, other benefits of ROME than monodispersity were identified. Particularly its suitability for the preparation of multiple emulsion is a subject emphasized in this thesis.

3.3.1 Primary emulsions

In order to produce stable multiple emulsions, the primary inner emulsion stability is of basic need. Small droplets are required to maintain a high yield during secondary emulsification. A monodisperse distribution is desirable to avoid Laplace pressure driven Ostwald ripening effects [145]. The production of the primary emulsion by rotating membrane device was considered. However, it was only possible to achieve the required small droplets sizes under certain conditions concerning the viscosity ratio between the two phases. Therefore, the primary W1/O emulsions were finally produced employing the rotor/stator device, the benefits of the ROME lie elsewhere.

To optimize emulsification time, samples were taken every minute and analyzed for the particle size distribution. The batchwise emulsiﬁcation by rotor/stator system Polytron using lipophilic surfactant PGPR usually led to bimodal distributions. In Fig. 3.4 the droplet size distributions after 5, 10, 15, and 20 min of emulsification for a W/O emulsion containing 5 wt% PGPR in the oil phase and 5 wt% NaCl in the aqueous phase are illustrated. We observed that after 5 min the emulsion displayed a monomodal distribution with droplet radii between 7 µm and 18 µm and a maximum at around 11 µm. After 10 min a second peak at
around 0.7 µm started to develop, increasing over time at the expense of the peak at larger diameters, until an almost monomodal distribution at smaller droplet radius was reached after 20 min. Therefore, the most suitable emulsification time for the standard system was determined to be 20 min. The energy input during the emulsification step was very high and the W1/O emulsion was strongly heated up.

![Graph showing particle size distribution](image)

Figure 3.4: Production of a 20/80 W1/O standard inner emulsion containing 5 wt% PGPR in the oil phase and 5 wt% NaCl in the aqueous phase. Particle size distribution after 5, 10, 15, and 20 min of emulsification using a rotor/stator mixer.

Using model food mixtures a similar trend in change of particle size against time was observed. The high percentage of salt in the inner aqueous phase (10 %) and the consequential decrease of interfacial tension (Chapter 4.3.1) led to a shift in particle size distribution towards smaller diameters. In Fig. 3.5 the median droplet size of various inner emulsions is plotted against emulsification time. The main droplet size reduction took place in the first 2 min of emulsification. The further droplet size decrease is quite small compared to the high energy input, therefore emulsification time was set to be 6 min for the food based emulsion. Fig. 3.5 also shows the influence of the PGPR content on the resulting droplet size. Due to the reduction in interfacial tension with increasing PGPR concentration (Chapter 4.3.1), droplets of the emulsion containing 5 % PGPR only were half the size compared to the one containing 1 % PGPR. The dependency between the amount of PGPR and the resulting median droplet size is shown in Fig. 3.6 (closed circles) for PGPR concentrations of 1, 2, 3, and 5 wt%. It is observable that the addition
of up to 5 wt% of PGPR in the oil phase leads to a decrease in median particle size for equal emulsification times. A PGPR addition of more than 5%, however, had no further effect on the droplet size.

Figure 3.5: Production of 30/70 and 50/50 W1/O model food emulsions containing 1 or 5 wt% PGPR in the oil phase and 10 wt% NaCl in the aqueous phase. Median drop size after 0, 2, 4, 6, and 8 min of emulsification.

As most experiments were designed to focus on only one parameter, for example the influence of the PGPR concentration on water transport, the connection between droplet size and surfactant concentration had to be considered. For these studies, all emulsions were prepared using only a small quantity of PGPR. The resulting droplet size was therefore rather large. After production, further PGPR was added in a second step under careful stirring, in order to avoid a further reduction in droplet size. Using this procedure we were able to obtain similar droplet sizes for W/O emulsions containing different amounts of PGPR as shown in Fig. 3.6 (open circles). Only 1% of PGPR was introduced prior to the emulsification step. The remaining 1, 2, 3, and 4% of PGPR respectively were added subsequently.

Emulsion stability against coalescence or flocculation was good over the investigated time of one month. Especially for high PGPR- and NaCl-contents, no changes in particle size distribution were detectable (Fig. 3.7). For low contents, first signs of destabilization were measurable by laser diffraction after two weeks, but were not visible in light-optical micrographs.
3 Multiple emulsions prepared by rotating membrane emulsification

Figure 3.6: Median drop size of W1/O model food emulsions as a function of different amounts of PGPR in the oil phase for two emulsification processes: entire PGPR added before emulsification (●); PGPR added in two steps (○).

Figure 3.7: Stability of a 20/80 W1/O standard emulsion containing 5 wt% PGPR in the oil phase and 10 wt% NaCl in the aqueous phase. Particle size distribution at production day and after 1, 7, and 30 d of storage.
3.3 Double emulsion preparation by rotating membrane

3.3.2 Reduced loss of enclosed aqueous phase during W/O/W production

During the secondary emulsification step in the production of W/O/W multiple emulsions, leakage of inner aqueous phase (W1) to the outer aqueous phase (W2) may occur due to mechanical stress. The leakage represents a loss of encapsulated substance and is therefore highly unfavorable. Presumably, a gentle emulsification process is beneficial for the preservation of the inner emulsion structure. In order to compare the rotating membrane to a continuous rotor/stator process, two different emulsions were produced by each device and the leakage during production was investigated.

![Droplet size distributions for W/O/W double emulsions produced by rotor/stator and rotating membrane, as well as for reference O/W emulsions. Multiple emulsions with phase ratio (20/80)-50/50 (left) and (50/50)-50/50 (right).](image)

Two standard emulsions with different amounts of inner aqueous phase (W1) in the oil phase were investigated. One double emulsions was produced with an inner emulsion of phase ratio 20/80 and the other one with an inner emulsion of phase ratio 50/50. The outer, secondary phase ratio was set to 50/50 for all multiple emulsions, in order to achieve a high viscosity for the rheological investigations. To compare the leakage caused by each device, the samples were analyzed rheologically, given the fact that leakage from the inner to the outer aqueous phase causes a decrease of the multiple emulsion viscosity. To prevent an influence of the particle size distribution on the measured viscosity [104], rotational speeds were set to achieve constant droplet sizes (Fig. 3.8). Viscosity curves were recorded for shear rates from 1 to 100 s⁻¹ using the double-gap couette cell at 20°C. To estimate the water amount lost from the inner aqueous phase, the viscosities of three different O/W reference emulsions were measured for phase ratios of 50/50,
45/55, and 40/60. The reference emulsions exhibited the expected shear-thinning behavior [104, 146], whereas the multiple emulsions showed Newtonian behavior over the measured range.

Viscosities for the multiple emulsions with lower inner phase ratio of 20/80 are shown in Fig. 3.9. The viscosity curves of both multiple emulsions, one produced by ROME and one produced by rotor/stator, showed the same behavior. They also had the same viscosity as the corresponding reference emulsion with a phase ratio of 50/50. Hence, it can be stated that the loss of inner aqueous phase was the same for both production methods and that hardly any leakage occurred during production.

Fig. 3.10 shows the viscosities of the multiple emulsions with heavier loaded oil droplets (inner phase ratio of 50/50). In this case, the viscosities of both multiple emulsions were significantly lower than the viscosity of the corresponding 50/50 reference emulsion. The multiple emulsion produced by ROME lay in the range of the 45/55 reference emulsion, whereas the viscosity decrease for the emulsion produced by rotor/stator system was considerably larger. A change in outer phase ratio from 50/50 to approximately 45/55 corresponds to a loss of about 20% of
the original W1 phase. The resulting viscosity of the multiple emulsion prepared by rotor/stator process in the range of the 40/60 reference indicates the loss of about 40% of the enclosed aqueous phase, which corresponds to a leakage twice as high as for ROME process.

Figure 3.10: Viscosity of (50/50)-50/50 multiple emulsions produced by ROME and by rotor/stator device Megatron, compared to O/W reference emulsions with phase ratios of 40/60, 45/55, and 50/50.

**Conclusion.** Both processes (Rotor/stator and rotating membrane) are suitable for the production of a multiple emulsion with small fractions of enclosed aqueous phase. The (20/80)-50/50 multiple emulsion was successfully produced by rotor/stator device and by ROME with hardly any leakage. Emulsions with a large fraction of internal water phase are more delicate. The rotor/stator system caused a considerable damage to the system, resulting in a loss of about 40% of the W1 phase. The rotating membrane device appears to be a more gentle technique where the induced loss was only about 20% of the inner aqueous phase. The impact of a gentle process seems to be marginal for low inner phase ratios, but becomes more relevant with increasing amount of enclosed W1 phase. Thus, the benefit of the rotating membrane device for the production of multiple emulsions was evidenced.
3.3.3 Concentrated emulsions

Schadler and Windhab [4] found that the disperse phase fraction of W/O emulsions produced by ROME has no influence on the resulting particle size distribution for disperse phase volumes between 5 and 30%. Even higher concentrated emulsions of 50 and 70% were produced and the existence of coalescence or other adverse effects such as phase inversion were investigated. For our experiments it was important to work at constant disperse phase volume flow in order to avoid a change in the dynamic of droplet detachment (i.e. dripping or jetting regime) [26, 30], while the flow rate of the continuous phase was adjusted so as to achieve the desired phase ratio.

Table 3.2: Median droplet sizes for O/W emulsions of phase ratios 50/50 and 70/30 for different rotational speeds.

<table>
<thead>
<tr>
<th>Rotational speed (rpm)</th>
<th>50/50 $x_{50,3}$ (µm)</th>
<th>70/30 $x_{50,3}$ (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6000</td>
<td>7.98</td>
<td>7.73</td>
</tr>
<tr>
<td>8000</td>
<td>5.14</td>
<td>4.77</td>
</tr>
<tr>
<td>10000</td>
<td>4.08</td>
<td>3.82</td>
</tr>
</tbody>
</table>

The two concentrated emulsions of type O/W, using ingredients for the food based emulsion system, were produced by ROME at three different rotational speeds. The resulting median droplet sizes are listed in Tab. 3.2. The median droplet sizes for the emulsion containing a higher disperse phase fraction were slightly smaller for all rotational speeds, and the droplet size distributions for the 70/30 emulsion showed a shift towards smaller droplet diameters. The polydispersity of the emulsions, i.e. the width of the distribution was compared by the span ($\text{span} = (d_{90,3} - d_{10,3}) / d_{50,3}$). The two emulsions showed similar span for each rotational speed. Thus, it can be stated that higher dispersed phase fractions have no adverse effect on emulsions produced by ROME and coalescence is not increased.

The decrease in droplet size for concentrated emulsion was probably caused by the change in viscosity. In the rotating membrane shear gap, the droplet phase concentration increases along the membrane. Therefore, a viscosity gradient in the shear gap occurs. Due to the higher total amount of disperse phase in the 70/30 emulsion, the viscosity gradient and with it the average viscosity in the shear gap was higher than for the 50/50 emulsion. An increased viscosity at constant shear rate $\dot{\gamma}$ leads to an increased shear stress $\tau$. Thus, the droplets detach earlier from

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3.4 Swelling of emulsions

The swelling-breakdown process in W/O/W emulsions, induced by electrolytes included in the inner aqueous phase, is controlled by several factors. Some of these factors, including lipophilic emulsifier concentration, electrolyte content, and phase ratios are discussed in this chapter. The diffusion process is schematically illustrated in Fig. 3.12. A ternary diagram is a barycentric plot including three variables. In Fig. 3.12 the three phases of a multiple emulsion are shown, which sum to a constant. The circle represents an example of an emulsion with phase ratio (20/80)-50/50, consisting of 10% inner aqueous phase, 40% oil phase, and 50% outer aqueous phase. The diffusion process, illustrated by the dashed arrow,
is a swelling process with water transport from W2 to W1 (left to right). The oil fraction remains constant, the diffusion of the water runs along the line indicating 40% of oil phase.

Figure 3.12: Ternary diagram displaying electrolyte driven water transport from the outer to the inner aqueous phase of a W/O/W emulsion. The oil fraction is remains 40%, while water diffuses from W2 and W1.

It is difficult to determine the extent of a diffusion process, since the diffusion usually is superimposed by a breakdown process due to bursting of the swollen double emulsion droplets (Fig. 2.4). A possible way to indicate the magnitude of diffused water is a rheological monitoring. The emulsion viscosity changes due to the expansion of the water-filled oil droplets and the depletion of the continuous aqueous phase leading to a highly concentrated secondary emulsion. Eventually, the diffusion process is slowed down by the electrolyte getting to the outer aqueous phase due to droplet breakdown or transport across the oil membrane. At some point, a pressure equilibrium is reached, the diffusion process stops and only breakdown takes place.
3.4 Swelling of emulsions

3.4.1 Rheological monitoring of emulsion thickening

Two different rheological methods were applied in order to observe the progression of the swelling-breakdown process. Employing oscillatory rheology (Chapter 2.3.4) a continuous measurement could be performed. The sample was filled directly from the outlet of the rotating membrane device into the cup of the Couette geometry, and the measurement was started within two minutes. Thus, the main part of the diffusion process could be monitored, and the most important changes in sample structure were visualized. Drawback of this method is the possible influence of the oscillation on the development of the sample structure.

![Graph showing comparison of emulsion swelling observed by oscillatory rheology and yield stress determination for two different multiple emulsions.](image)

Figure 3.13: Comparison of emulsion swelling observed by oscillatory rheology (open symbols) and yield stress determination (closed symbols) for two different multiple emulsions. The secondary emulsions with phase ratio 50/50 for both emulsions, primary phase ratio 50/50 (triangles) or 30/70 (circles). Food model system containing 5% PGPR.

The yield stress method (Chapter 2.3.3), in contrast, is a non-continuous method. Samples were taken into plastic cups, and for each measurement a new sample was used. However, the yield stress method did not allow the continuous observation of the process and a minimum time of about 5 min between the measurement of two data points was needed. For some samples, the change in sample structure was almost completed before the first yield stress was measured.
In order to verify the oscillation method, the two tests were conducted simultaneously for samples of the same multiple emulsion batch. In Fig. 3.13 the storage modulus \( G' \), obtained from oscillatory measurement during 150 min, is compared to fitted yield stresses, which were measured every 5 min using the rotating vane method. The progression of the curve is very similar, therefore we assume, that both methods characterize the same structural interactions. The yield stress signals show a slightly faster increase, resulting earlier in a plateau. The deviations can be explained by the instability of the yield stress signal. The yield stress determination is a continuing measurement, taking up to 5 min to collect one single data point. In the first minutes, the samples underwent rapid changes. In this period, the oscillatory method has the better resolution. Based on this, and on the fact, that the oscillatory method provides additional structure information through the loss modulus \( G'' \), most measurements were performed using oscillatory rheometry.

### 3.4.2 Role of PGPR in swelling emulsions

Primary emulsions of the multiple emulsions investigated in this section were produced in a two step process (see Fig. 3.6) in order to achieve droplets of the same average size, independent from PGPR content. Fig. 3.14 shows the development of the storage modulus \( G' \) for four multiple emulsions with varying PGPR concentration over time. The emulsions of of standard system type contained 0.5, 1, 2.5, or 5 wt% of PGPR in the oil phase, and had a quite low NaCl content of 0.5 wt% in the inner aqueous phase. The initial phase ratio was (20/80)-50/50.

The PGPR content had an influence on the beginning of the sample solidification. The transition of the sample behavior from viscoelastic fluid \( (G'<G'') \) to viscoelastic solid \( (G'>G'') \) was observed rheologically. The more PGPR in the emulsion, the faster \( G' \) increased to a value larger than \( G'' \), i.e. the sooner the sample displayed the behavior of a viscoelastic solid. For 5 wt% of lipophilic surfactant, this transition was observable after 1.5 min only. For an emulsion with only half the PGPR concentration, it took more than twice as long (4 min). The storage modulus of both samples was increasing for the entire period investigated, reaching no peak value in the given time. A leveling-off, however, was recognizable. This indicates the beginning of a breakdown process superimposing the swelling process.
A higher PGPR concentration led to higher swelling degrees (i.e., higher $G'_{\text{max}}$) of the multiple emulsions. This is probably due to the additional surfactant available for the stabilization of newly generated interface, thus inhibiting coalescence between the growing W1 droplets and the continuous W2 phase.

For the emulsion containing only 1 wt% of PGPR, the swelling started later (after 5.3 min), and the breakdown commenced sooner. Hence, a maximum $G'$ was reached in the investigated time. After this maximum, breakdown dominated the progression of $G'$. For the sample with very low surfactant concentration (0.5 wt%) this effect was even more pronounced. Observable emulsion swelling began not until 10 min after the production of the emulsion, and was soon dominated by the breakdown. The transition to $G'>G''$ took place after 15 min and was reversed 80 min later. Before the end of the measuring period, the storage modulus was not detectable anymore, indicating an almost complete breakdown of the multiple emulsion. The samples stored for the long term stability measurements showed signs of separation within the first 24 h. The multiple emulsions containing more PGPR, however, maintained their viscoelastic solid characteristics for the entire measuring period of 4 weeks.

The decrease in $G'$, calculated by $(G'_{\text{max}} - G'_{1m}) / G'_{\text{max}}$, was lower, the more PGPR was included. The first two samples lost only 37% and 48% respectively, whereas the samples with lower surfactant content lost 83 wt% and 100%, respectively, in $G'$. This superior stability can be due to the stabilizing effect of the PGPR during storage. On the other hand, the increased stability also can be a consequence of the PGPR inhibiting leakage during the swelling process leading to higher viscosity and the depletion of water in the continuous phase of the sample. This factors prevent destabilizing factors as creaming or drainage leading to higher storage stability.

For the food based emulsion systems, high NaCl contents of 10% were used. This amount led to a fast emulsion swelling, the process was already completed at the time the samples discharged from the ROME device. Therefore the yield stress method was appropriate, there was no need for monitoring of the first few minutes. The samples were analyzed for their yield stresses after 3 hours, one day, and one week. Fig. 3.15 shows the obtained yield stresses plotted against the PGPR concentration in the oil phase. Initial phase ratio of these samples was (50/50)-50/50.

An increase in PGPR up to 5 wt% led to an increased yield stress. Further surfactant addition had no effect on the examined sample characteristics. Low PGPR samples showed an apparent increase in yield stress during the first week. These emulsions displayed visible signs of destabilization due to drainage of the continuous phase. Drainage of the W2-phase led to a concentration of the remaining
Figure 3.14: Comparison of emulsion swelling. Emulsions of standard system type, containing 0.5 wt% NaCl and 0.5, 1, 2.5, or 5 wt% of PGPR. Continuous oscillatory measurement during the first two hours; storage tests after 1 d, 2 d, 1 w, 2 w and 4 w. Initial phase ratio of (20/80)-50/50.

Figure 3.15: Comparison of emulsion swelling using yield stress determination. Emulsions of model food system type, containing 10 wt% NaCl and 1, 2, 3, 4, 5, or 7.5 wt% of PGPR. First measurement conducted 3 h after production; storage tests after 1 d and 1 w respectively. Initial phase ratio of (50/50)-50/50.
3.4 Swelling of emulsions

emulsion, in the storage beakers a thin water layer at the bottom evidenced the separation. The rheometer geometry used to determine the yield stress was only immersed in the concentrated emulsion. Therefore, a seemingly increased yield stress was detected. Presumably, the increased yield stress and stability of the emulsions with high PGPR contents again resulted from the ability to stabilize the new interface created by the diffusion of the water. The more surfactant molecules available, the more interface could be stabilized. We assume the increase from 5 to 7.5 wt% PGPR yields no additional benefit because the water available for diffusion was depleted already for the 5 wt% PGPR sample. Probably for both samples no coalescence between W1 droplets and the continuous phase took place. Only a very thin water film containing the hydrophilic surfactant remained between the swollen oil droplets, and no better stabilization was possible by the addition of further PGPR.

The higher stability of emulsions containing more lipophilic surfactant is not only caused by the superior stabilization of the interface generated due to the swelling. We assume that PGPR stabilizes the primary emulsion during the secondary emulsification step, preventing loss of inner aqueous phase at this stage already. Early leakage of W1 phase causes an lower initial NaCl gradient and a state of equilibrium is reached faster during the swelling process. The depletion of the continuous water phase additionally leads to a concentration of the leaked electrolyte. Breakdown caused by swelling, releasing NaCl, does not necessarily have to take place in order to develop a balanced state, if NaCl is already present in the continuous phase.

Figure 3.16: Fitted yield stress for multiple emulsions of model food system type, containing 2.5% PGPR (left) or 5% PGPR (right) respectively, plotted against the phase ratio of the secondary emulsion. Yield stresses measured 3 h, 1 d, and 1 w after production of the samples, primary emulsion phase ratios of (50/50) for all samples.
In the above experiments, the free surfactant, i.e. the amount of surfactant added after the mixing in the production of primary emulsions, was varied. This led to variations in the size of the total resulting W1/O interface. In a second series of experiments, the PGPR concentration in the oil phase was kept constant, but the phase ratio of the secondary emulsion was varied. Thus, the overall content of PGPR in the multiple emulsion was varied as well. In Fig. 3.16 the fitted yield stress is plotted against the phase ratios of the secondary emulsion. The samples contained 2.5 wt% PGPR (Fig. 3.16 left) or 5 wt% PGPR (Fig. 3.16 right), respectively, with a phase ratio of the primary emulsion of (50/50). An increasing secondary phase ratio (from left to right) represents a decrease in continuous aqueous phase available for diffusion. Furthermore, it results in an increase of the overall oil and PGPR content and in an increase of the overall inner aqueous phase content including the salt, respectively.

Emulsions containing 5 wt% PGPR exhibited a distinct maximum yield stress for a phase ratio of 30/70. Interestingly, an increasing amount of dispersed phase, and hence increasing PGPR contents in relation to the entire emulsion, led to a decrease in the yield stress. With the leakage of the electrolyte the following theory is proposed: Emulsions with high phase ratio (i.e. high dispersed phase fraction) contain higher quantities of inner aqueous phase, and consequently, higher quantities of NaCl. If during the formation of each droplet the same amount of inner aqueous phase is lost, the amount of NaCl leaked to the continuous phase during the secondary emulsification step is considerably higher for emulsions with high dispersed phase fractions. Due to the resulting high electrolyte concentration in the continuous phase, a state of equilibrium is reached sooner, less swelling occurs, and more water remains in the continuous phase, leading to lower yield stresses. We assume that for the emulsion containing 5 wt% PGPR which exhibited a maximum yield stress, almost the entire continuous phase water content available for diffusion was depleted and diffused to the W1 droplets where they were stabilized through the PGPR. The decrease in yield stress for emulsions containing even less dispersed phase (in Fig. 3.16 the samples to the left of the emulsion with maximum yield stress) can be explained by breakdown. Too much continuous water phase was available and the overall PGPR content was too low to stabilize the large, additionally generated interfacial area.

Generally emulsions containing 2.5 wt% PGPR lead to lower yield stresses because more inner aqueous phase is lost during production. The maximum observed for this series of experiments was not as pronounced, yet it existed for a phase ratio of 50/50. The maximum yield stress occurred for phase ratios with a higher dispersed phase fraction. This was probably due to the lower amount of PGPR available to stabilize the swelling inner water droplets. The low-surfactant emulsions, therefore, were more susceptible to breakdown.
The results are supported by the observations performed by confocal laser scanning microscopy. In Fig. 3.17 the confocal scanning laser micrographs containing 5 wt% PGPR (top) or 2.5 wt% PGPR (bottom) with secondary emulsion phase ratios of 50/50 (left) or 30/70 (right) are shown. Bright areas contain the fluorescent marker Nile red and are considered lipophilic. Large oil droplets are darker towards the center. This gradient was caused by the slow diffusion of the fluorescent marker. The top right picture shows the 5 wt% PGPR 30/70 emulsion. This sample exhibited the highest yield stress. It is in evidence that the oil droplets in this sample were larger than in all the other samples. The reason for this is on the one hand the large amount of water per inner emulsion available for diffusion. On the other hand the above discussed smaller amount of NaCl leaked from the inner aqueous phase during production leads to more diffusion and therefore larger droplets. Droplet size in the top left sample (5 wt% PGPR/50/50) was considerably smaller. Besides the smaller amount of water available for diffusion and the higher NaCl leakage during production, the larger number of droplets available to absorb the water prevented the formation of big droplets. The emulsions with higher surfactant concentration (top right and left) are more densely packed than the samples containing only 2.5 wt% PGPR. Therefore, less water remained in the continuous phase. This indicates a higher NaCl content in the continuous phase, either due to more leakage during production or due to more breakdown. The low-surfactant samples appear to be very similar in droplet size and packing density. This is confirmed by the similarity of the yield stress measured for the two samples (Fig. 3.16).

Conclusion. The main role of PGPR is the stabilization of additional interface, generated by the growing internal W1 water droplets. The more PGPR in the oil phase, the longer these W1 droplets are protected from coalescence with the surrounding W2 phase. A maximum beneficial PGPR concentration of 5 wt% was found using the model food emulsion. Further surfactant addition had neither beneficial nor adverse effects on the diffusion and stability.

The protection of the inner aqueous phase during the secondary emulsification step is also an important function of the PGPR. Leakage of the W1 phase to the continuous phase during production has a strong impact on the swelling capacity of the sample. Presumably PGPR plays a role in water transport. A certain influence on the swelling speed was also detectable. The insufficient long term stability and the drainage occurring in the samples with less PGPR are the consequence of the high leakage during the swelling process. The higher viscosity and the depletion of water in the continuous phase of the PGPR rich samples prevent drainage or creaming and therefore are the reason for the superior stability.
Figure 3.17: Confocal laser scanning microscopic pictures of four food based emulsions containing either 5 wt% PGPR (top) or 2.5 wt% PGPR (bottom), with secondary emulsion phase ratios of 50/50 (left) or 30/70 (right). CLSM micrographs were taken 3 hours after emulsion production (Magnification: 400 times).
3.4 Swelling of emulsions

3.4.3 Electrolytes and water transport

In order to investigate the influence of the electrolyte, multiple emulsions with constant surfactant content and varying electrolyte content were produced. We observed that samples with high amounts of salt in the inner aqueous phase displayed already a high viscosity at the discharge of the rotating membrane and, therefore, a fast swelling. Accordingly, a strong influence of the NaCl on the transport velocity was supposed, and thus, the oscillatory method was chosen in order to monitor the process during the first few minutes.

Fig. 3.18 shows the development of the storage modulus $G'$ for four multiple emulsions with various NaCl concentrations over time. The emulsions of standard system type contained 1, 2.5, 5 or 10 wt% of NaCl in the W1 phase and had a high PGPR content of 5 wt% in the oil phase in order to avoid early breakdown. The initial phase ratio was (20/80)-50/50. It emphasized that the NaCl content, as the surfactant content, also had an influence on the beginning of the sample solidification. Solely for the emulsion with the lowest salt content of 0.5 wt%, a transition $G'<G''$ to $G'>G''$ was observed. In case of the other samples this transition took place before the measurement was started. Correspondingly, the maximum values for $G'$ were reached earlier for samples with higher electrolyte content. The emulsion containing a high NaCl content of 5 wt% displayed the maximum measured value for $G'$ at the beginning of the experiment. The sample with a low NaCl content of 0.5 wt%, in contrary, achieved its maximum storage modulus at the very end of the measurement, after 120 min.

An influence of the concentration on the diffusion rate was expected due to the increase of the osmotic pressure (Eq. 2.8). Unexpectedly, the electrolyte content also had a beneficial effect on the emulsion swelling, higher $G'$ were achieved for increasing NaCl contents. A possible reason for this is the smaller droplet size achieved for the inner emulsions with higher NaCl concentration. A certain influence of the electrolyte on the interface was proved due to the interfacial tension which was considerably lowered by the addition of NaCl (Chapter 4.3.1). However, the smaller droplets with consequentially higher Laplace pressure were less susceptible to leakage during the secondary emulsification and led, therefore, to a more complete depletion of the outer water phase due to diffusion.

The breakdown during storage, calculated by $(G'_{max} - G'_{1m}) / G'_{max}$ was not influenced by the addition of more electrolyte, in contrary to the findings for a change in PGPR content. The decrease from $G'_{max}$ to $G'$ after one month was approximately 35% for all samples, therefore, the electrolyte had no influence on the long term stability.
Figure 3.18: Comparison of emulsion swelling. Standard emulsions containing 5 wt% PGPR and 0.5, 1, 2.5, or 5 wt% of NaCl. Continuous oscillatory measurement during the first two hours, storage tests after 1 d, 2 d, 1 w, 2 w, and 4 w. The initial phase ratio was (20/80)-50/50.

Figure 3.19: Comparison of emulsion swelling. Emulsions of model food type, containing 2.5 (open symbols) or 5 wt% PGPR (closed symbols) respectively, and 1, 5 or 10 wt% of NaCl. Continuous oscillatory measurement for 150 min. Initial phase ratio of (50/50)-50/50.
For the food based emulsion systems, short term experiments using oscillatory rheology were performed. Additionally to the samples with the usual high NaCl content of 10 wt%, samples containing 1 and 5 wt% NaCl were produced for two PGPR concentrations of 2.5 and 5 wt%, respectively. Initial phase ratio of all these samples was (50/50)-50/50. In Fig. 3.19 the storage moduli $G'$, measured during the first 150 min, are plotted versus time. The influence of the electrolyte on the storage modulus in the food system cannot easily be compared to the standard system, because no maxima were reached in the observed period. The only exceptions were the emulsions containing 10 % NaCl. For these systems a leveling-off (2.5 wt% PGPR) or a maximum $G'$ value (5 wt% PGPR) was found.

The high electrolyte content of 10 wt% clearly had adverse effects on the swelling behavior. Possibly, the swelling rate was too fast to allow a proper stabilization of the newly generated surface, thus causing breakdown and a deceleration of the swelling process. The effect of the electrolyte concentration on the resulting storage modulus was the same for both PGPR concentrations: the swelling improved with increasing NaCl content from 1 to 5 wt%, and worsened again with further increase to 10 wt% NaCl. In Chapter 4.3.1 we observed that an increase in NaCl concentration from 5 to 10 wt% only led to a small further decrease in interfacial tension.

**Conclusion.** We assume that the main influence of the electrolyte is the increase of the diffusion rate. This behavior was expected due to the considerably higher osmotic pressure. According to Eq. 2.8, the osmotic pressure increases linearly with the molar concentration of the solution. Less expected was the influence of the NaCl on the magnitude of the swelling. For two different PGPR concentrations and for two phase ratios, an increase in NaCl led to higher storage moduli and, therefore, to stronger swelling and less breakdown. We suggest that this behavior is based on the smaller W1 droplets which are caused by the decrease in interfacial tension due to electrolyte addition. Smaller droplets are more stable during secondary emulsification. Therefore, leakage to the continuous phase is prevented. Yet, an addition of very high amounts of NaCl had an adverse effect on the emulsion swelling due to a too fast swelling rate to allow the stabilization of the newly generated interface.
3 Multiple emulsions prepared by rotating membrane emulsification

3.4.4 Inner phase ratio influencing water diffusion and emulsion breakdown

Multiple emulsions of model food type were produced with different primary emulsion phase ratios of (30/70) and (50/50). The droplet size distributions of the primary emulsions were similar. The secondary emulsion phase ratio was 50/50 for all samples. Both types were produced for PGPR contents of 1 and 5 wt%. The samples with higher phase ratio of (30/70), containing a higher amount of oil within the inner emulsion, displayed a higher yield stress for both PGPR contents. Two factors are contributing to this: (i) The higher loss of inner aqueous phase during production for (50/50) primary emulsions (Chapter 3.3.2). Therefore, a higher amount of electrolyte leaked to the continuous phase leading to an earlier termination of the swelling process and, thus, to lower yield stress. (ii) A lower phase ratio of the primary emulsion is equivalent to a higher overall PGPR content. The same amount of continuous aqueous phase was available for diffusion, but the primary emulsion provided more oil and PGPR to stabilize the diffused water. Therefore, earlier breakdown might have occur for the (50/50) primary emulsion leading to lower yield stresses.

The storage stability of the (30/70) primary emulsion was expected to be higher, due to the higher overall amount of PGPR available for stabilization. However, for both emulsifier concentrations, this sample proved to be less stable. This trend is not easily explicable, but a possible approach is based on the size of the inner water droplets. Due to the smaller W1 fraction, less droplets are formed in the (30/70) primary emulsion. Therefore, the entire amount of diffused water has to be shared between a smaller number of droplets, which consequentially swell up to larger droplet sizes. The faster sedimentation, caused by the larger water droplets, is be a possible reason for the decreased storage stability.

3.5 Conclusions

In order to produce stable multiple emulsions, the inner emulsions are of great importance. A process was developed to match the requirement of small and as uniform as possible droplets. The emulsions were produced batchwise by rotor/stator device. A small droplet size was achieved by a long emulsification time. A further decrease in droplet size was only achievable by the addition of more
3.5 Conclusions

Figure 3.20: Influence of primary emulsion phase ratio. Comparison of fitted yield stresses of emulsions containing 1 or 5% PGPR, and primary emulsion phase ratios of (30/70) (closed symbols) or (50/50) (open symbols) respectively. Fitted yield stresses measured after 3h, 1d, and 1w. Emulsions of food system type with initial secondary phase ratio of 50/50 for all samples.

PGPR to the oil phase and more NaCl to the inner aqueous phase. A two phase emulsification process was developed in order to achieve emulsions with equal droplet sizes independent from the PGPR content of the emulsion.

For the secondary emulsification step, i.e. the production of the multiple emulsion, a rotating membrane device was employed. In order to prove the gentleness of the process, multiple emulsions produced by ROME were compared to samples produced by continuous rotor/stator emulsification. The resulting multiple emulsions were characterized rheologically and their viscosities were compared to the viscosities of simple reference emulsion systems of known phase ratio. Both processes turned out to be suitable for the production of a multiple emulsion with small share of enclosed aqueous phase. The (20/80)-50/50 multiple emulsion was successfully produced by rotor/stator device and by ROME with hardly any leakage detected. Emulsions with a large internal water phase fractions of (50/50) turned out to be more delicate. The rotor/stator system caused a considerable damage to the system, resulting in a loss of 40% of the W1 phase. The rotating membrane device appears to be more gentle, the induced loss was only 20% of W1. The impact of a
gentle process seems to be marginal for low inner phase ratios, but becomes more relevant as the enclosed W1 phase is increased. Thus, the benefit of the rotating membrane device for the production of multiple emulsions could be evidenced.

A further benefit of the rotating membrane device was the production of emulsions with high dispersed phase fractions. Emulsions containing 50 or 70% of dispersed phase were produced without increase in coalescence between droplets in the shear gap. The resulting median droplet size even decreased for the higher concentrated emulsion, for all three rotational speeds investigated. This decrease was presumably caused by the change in viscosity, leading to an increased shear stress within the shear gap of the rotating membrane. Therefore, the droplets were sheared off earlier from the pores.

A possible way for the production of highly viscous emulsions with a low fat content is the so-called 'swelling process'. Furthermore, substances encapsulated in W/O/W emulsions are released by swelling-breakdown. In this process, water transport from the continuous phase to the inner aqueous phase is induced by an osmotic gradient. The water influx causes the droplets to grow (swelling) until coalescence between the swollen W1 droplets and the continuous W2 phase (breakdown) occurs. The swelling-breakdown was monitored via the thickening of the emulsions due to depletion of the continuous phase. Two different rheological methods were applied, yield stress determination and oscillatory rheology. Both methods were suitable to investigate the swelling process, although oscillatory rheology provided more structure information and had the better resolution for short time tests.

The influence of PGPR on the swelling-breakdown behavior was investigated for both, the standard system and the model food emulsion. Two main functions of PGPR were identified: the stabilization of additional interface, generated by the growth of the internal W1 water droplets, and the protection of the inner aqueous phase during the secondary emulsification step in order to avoid a W1 loss at this stage. For very low surfactant concentrations, almost no thickening occurred. Newly formed interfaces could not be stabilized due to deficient surfactant concentration and breakdown soon superimposed the swelling. A minor influence of the PGPR concentration on the diffusion rate was observed. We assume that water transport occurs mainly through a mechanism which does not require much free surfactant molecules. A layer of surfactant at the interface seems to be sufficient.

The influence of the electrolytes on the diffusion rate was much more pronounced.
3.5 Conclusions

Even with a very small percentage of NaCl, emulsion thickening was induced. However, the maximum viscosity was achieved much later than for samples with high NaCl concentrations. This effect of the electrolyte was expected. It is well known that the osmotic pressure increases linearly with the molar concentration of the solution. The influence of the electrolyte on the magnitude of swelling was less expected. Increased NaCl contents led to higher measured storage moduli and with it to more swelling. The reason for this behavior is, that the electrolyte affects the stabilization of the inner droplets during the secondary emulsification step and, therefore, prevents leakage at this stage.
4 Facilitated water transport across an oil membrane

4.1 Introduction

To get a better understanding of processes involved in the swelling-breakdown of W/O/W double emulsion systems, the focus in this chapter was laid on actions at and close to the interface. Interfacial tensions of systems containing different quantities of PGPR in the oil phase in combination with different NaCl solutions were measured using pendent drop tensiometry. Furthermore, the influence of these substances on interfacial elasticity was investigated by oscillatory tensiometry. The migration of the lipophilic surfactant PGPR to the aqueous phase could be observed, and spontaneous emulsification occurring at interfaces of oil/water systems containing PGPR was studied and confirmed to be a mechanism for water transport.

A model double emulsion droplet consisting of an inner water phase surrounded by a thin oil film was formed in the continuous aqueous phase using a purpose-built double capillary setup. Water transfer across the oil layer as a function of electrolyte and surfactant concentration was investigated. For systems containing PGPR a local thinning of the oil layer was observed, causing the rate of water diffusion to increase by more than an order of magnitude. This behavior was explained by different transport mechanisms.
4.2 Experimental

4.2.1 Materials

A similar system was used as in the previous chapter. The aqueous phase was mainly made of water, purified with a Millipore ‘Direct-Q 3’ ultrapure water system (Millipore, USA). As electrolyte, common table salt (JuraSel Speisesalz, Schweizer Rheinsalinen, Switzerland) was used, consisting of at least 99.8% sodium chloride. The oil phase was made of commercially available sunflower oil (Florin AG, Switzerland) extracted from sunflower seeds and used without additional purification (see Tab. 3.1). As a lipophilic emulsifier, Grindsted PGPR 90 (Danisco AG, Denmark) was used as received (Molecular structure depicted in Fig. 2.8).

4.2.2 Tensiometry

**Drop tensiometer.** A drop tensiometer built in our laboratory [147, 148] was used to measure surface and interfacial tension. The method used in this work is based on a numerical fitting procedure of the Laplace equation to a drop profile. For the interfacial tension measurements, drops (or bubbles for surface tension measurements respectively) were formed at the tip of a reverse stainless steel capillary of 1.48 mm diameter, connected to a gas-tight precision syringe (Hamilton, Switzerland) and immersed into the continuous phase in a cuvette. The syringe containing the oil phase and the cuvette containing the aqueous phase were thermostatted at 20°C using a circulating water-bath. Images of the drop profile were acquired using the CCD camera Sony DFW-500 (Sony, Japan) operated at one or two frames per minute during the interfacial tension measurement. The photographically recorded drop profiles were fitted using a software algorithm developed in our laboratory running on Matlab platform, which calculates the radius of curvature in drop apex, the capillary constant (and with it the interfacial tension), the drop surface, and the drop volume.

**Profile analysis tensiometer PAT1.** For the oscillatory tensiometric measurements the Sinterface Profile Analysis Tensiometer PAT1 (Sinterface Technologies, Germany) with an inverse capillary (2 mm diameter) was used. The set-up of the
4.2 Experimental

The instrument consists of a dosing system with capillary, a measurement cell, and a CCD camera with objective. For all oscillatory measurements a sunflower oil drop containing various amounts of PGPR was measured against water containing various amounts of NaCl. The measuring cell was filled with water before the insertion of the capillary. A drop of defined volume (7 mm$^3$) was formed and oscillatory measurement was started after the interfacial tension had reached equilibrium. An amplitude of 0.5 mm$^3$ was applied for frequencies between 0.02 and 0.6 Hz. The recorded drop profiles were fitted by PAT1 software. Thus received data for interfacial tension and drop interfacial area were fitted with a sinusoidal function using MS Excel to determine the amplitude and phase for a given frequency.

For harmonic area changes, the dilatational modulus is a complex quantity composed of a real part $E'$ (storage modulus) and an imaginary part $E''$ (loss modulus):

$$E^*(\omega) = E' + iE''$$  \hspace{1cm} (4.1)

for a deformation frequency $\omega$. If $E^*$ is measured in an experiment applying small sinusoidal changes in surface area, it can be described analogous to bulk rheology by the interfacial tension response $\Delta\sigma$ to the relative oscillatory area changes $\Delta A/A_0$ of the oil/water interface [149–151].

$$|E^*| = \frac{\Delta\sigma}{\Delta A/A_0}$$ \hspace{1cm} (4.2)

Thus, interfacial tension and interfacial area functions gained from oscillatory tensiometric measurement enabled the calculation of $|E^*|$. 

Table 4.1: Densities utilized for drop profile fitting.

<table>
<thead>
<tr>
<th>Water</th>
<th>Sunflower Oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>% NaCl</td>
<td>Density (g/cm$^3$)</td>
</tr>
<tr>
<td>0</td>
<td>0.998</td>
</tr>
<tr>
<td>1</td>
<td>1.012</td>
</tr>
<tr>
<td>5</td>
<td>1.033</td>
</tr>
<tr>
<td>10</td>
<td>1.071</td>
</tr>
</tbody>
</table>

**Density determinations.** Densities of the respective phases for the tensiometric measurements were conducted at 20°C by Paar DMA-38 density meter (Anton Paar GmbH, Austria) using the oscillating U-tube method. Densities utilized for tensiometric measurements are shown in Tab. 4.1.
4 Facilitated water transport across an oil membrane

4.2.3 Double capillary

**Setup.** In order to form a model double emulsion droplet at a double capillary two drop tensiometers (as described in Chapter 4.2.2) were utilized. The first was used for the control of the inner aqueous phase, the second for the control of the oil phase. The drop volume resolution, i.e. the smallest measurable volume increment was 0.01 µl for the oil phase and 0.02 µl for the aqueous phase. The double capillary was built from two stainless steel tubes, one having an inner diameter of 2.7 mm and the other having an outer diameter of 2 mm (Hamilton, Switzerland). The smaller tube was precisely centered in the larger one in order to obtain a symmetric liquid flow in the gap, resulting in a gap width of 0.35 mm. To avoid wetting problems at the outer tube if sessile drops of SFO/PGPR solutions were formed the inverted capillary setup was chosen (capillary tip pointing upwards, see Fig. 4.1).

![Figure 4.1: Close-up of the double capillary setup: oil phase inlet (1), tip of the double capillary with droplet (2), inlet for the inner aqueous phase (3), thermostatted cuvette containing continuous phase (4), syringe containing inner aqueous phase in thermostatted syringe holder (5).](image)

**Drop formation.** In order to form an oil layer around the water droplet, the gap of the double capillary was filled with the oil phase. The inner capillary was not entirely filled with liquid. Some air was left in the inner capillary to prevent mixing of the inner and the outer aqueous phase before the generation of oil layer separating these two phases. Thus prepared, the double capillary was immersed
into the cuvette containing the 'continuous' outer aqueous phase. The air from the inner capillary was then pressed out, and the inner capillary was immediately covered by oil drop ejected through the double capillary gap. The first oil drop was detached, the oil remaining on the tip of the outer capillary and over the gap was reduced to the desired amount by sucking it back into the gap. This oil was then inflated by a defined amount of inner aqueous phase, which was pumped into the droplet through the inner capillary (Fig. 4.2).

Figure 4.2: Schematic drawing of the formation of a double emulsion model droplet. Formation of oil droplet immediately after removal of air from the inner capillary (A), detachment of oil droplet (B), sucking back of the excess oil through the outer capillary (C), inflating of the remaining oil by inner aqueous phase through the inner capillary (D).

The thus formed model drop was observed for several hours until either diffusion led to an almost complete drainage of the inner aqueous phase, or rupture of the oil film and consequential loss of the inner water phase occurred. Images of the drop were acquired every 10 s during the lifetime of the drop, using a Sony DFW-500 CCD camera (Sony, Japan) and a 55 mm Micro Nikkor objective (Nikon, Japan).
4.3 Properties of the oil-water interface

4.3.1 Interfacial tension

To get a better understanding of the influence of the lipophilic emulsifier PGPR and electrolyte NaCl on the properties of an oil/water interface, interfacial tensions (IFT) of simple W/O systems were measured. Oil droplets containing 0, 1, 5, or 10 wt% of PGPR were formed into an surrounding aqueous phase containing 0, 1, 5, or 10 wt% NaCl.

![Figure 4.3: Interfacial tensions after 60 min of equilibration plotted against PGPR concentration in sunflower oil for NaCl concentrations of 0, 1, 5, and 10% in the aqueous phase.](image)

For the pure oil/water system without any surfactant or electrolyte a slow decrease of the IFT with time was observed, leading to an equilibrium at 23 mN/m. The decrease is attributed to surface active components in the sunflower oil such as free fatty acids (see Chapter 3.2.1). The addition of high amounts of salt to the aqueous phase led to lower IFT (21.5 mN/m for 5 wt% of NaCl) and to a longer equilibration time.

In Fig. 4.3 the interfacial tensions (after 60 min of equilibration) for different salt concentrations in the aqueous phase are plotted against the PGPR concentration
in the oil phase. The values are the average of three measurements, standard deviations are given within the size of the symbols. The addition of salt to the water resulted in a IFT decrease for any given PGPR concentration. Although this effect was less pronounced without PGPR it became dominant for systems with emulsifier present in the oil phase. High salt concentrations of 10 wt% led to interfacial tensions lower than 1 mN/m for all emulsifier concentrations investigated.

Compared to the effect on ionic surfactants the addition of salt has a relatively small impact on nonionic surfactants [152]. However, the lyotropic salt NaCl is known to reduce the solubility of nonionic surfactant in water [153, 154]. The decreased surfactant solubility leads to an increased adsorption at the interface, and therefore to a reduced interfacial tension [155]. PGPR is mainly oil soluble, but its solubility in the aqueous phase could be evidenced (Chapter 4.3.3). We assume that the salting-out effect of PGPR from the aqueous phase by the electrolyte NaCl leads to a decreased IFT.

The addition of lipophilic surfactant PGPR to the oil phase caused a strong reduction of the IFT already in a low concentration of 1 wt%. Further addition of PGPR had no IFT decreasing effect. At high PGPR concentrations a slight increase of interfacial tension for all systems containing electrolyte was observed. However, higher surfactant concentrations led to a faster IFT decrease and more rapid equilibration. We assume that all PGPR concentrations are sufficient to cover the entire oil/water interface. Higher PGPR concentrations, however, are leading to faster occupation of the interface due to the higher availability of surfactant molecules.

### 4.3.2 Interfacial elasticity

The interfacial film has a strong potential impact on water transport. Rigid or highly viscous interfaces may hinder diffusion or influence emulsion stability [1, 7–9]. Thus, the interfacial elasticity depending on emulsifier and electrolyte content was investigated by dilatational interfacial rheology using the oscillating pendent drop method.

Interfacial properties were characterized by the dilatational modulus $|E^*|$ measured under oscillatory area changes $\Delta A/A_0$ at the oil/water interface leading to an interfacial tension response $\Delta \sigma$ (Eq. 4.2). A strong interfacial tension response (i.e. a high amplitude for the sinusoidal interfacial tension function) per change in drop surface represents higher interfacial elasticities.
4 Facilitated water transport across an oil membrane

No influence of the electrolyte on the interfacial elasticity was observed. In Fig. 4.4 the dilatational modulus $|E^*|$ for varying NaCl concentrations is plotted against the oscillation frequency. For the oil/water interface containing 5 wt% PGPR in the oil phase no change in dilatational modulus occurred as a result of NaCl addition. The resulting dilatational moduli were in the same range for all investigated electrolyte concentrations, but increased for increasing frequencies.

![Graph showing the effect of varying salt concentration on the interfacial dilatational modulus $|E^*|$ of the W/O interface plotted against the frequency. NaCl concentrations 0, 0.5, 1, 2.5, and 5 wt% in the aqueous phase, PGPR concentration of 5 wt%]

Figure 4.4: Effect of varying salt concentration on the interfacial dilatational modulus $|E^*|$ of the W/O interface plotted against the frequency. NaCl concentrations 0, 0.5, 1, 2.5, and 5 wt% in the aqueous phase, PGPR concentration of 5 wt%.

Higher oscillation frequencies yielded higher $|E^*|$ for all oil/water systems investigated. In contrast to the electrolyte, the surfactant PGPR showed a distinct influence on the interfacial elasticity. Starting with the oil/water system without surfactant, the addition of PGPR up to the maximum investigated concentration of 5 wt% systematically decreased the dilatational modulus (Fig. 4.5). Therefore, the interfacial elasticity measured by dilatational rheology was lowered by PGPR. We suggest that the surface active substances naturally occurring in suflower oil were displaced from the interface by the increasing amount of PGPR molecules. It is possible that these substances possess a stronger tendency to form an elastic interfacial film than the PGPR. High concentrations of PGPR were shown to lead to a faster decrease of the IFT and therefore to a higher coverage of the interface.
4.3 Properties of the oil-water interface

4.3.3 Migration of PGPR to the aqueous phase

PGPR is a highly lipophilic substance specified as "insoluble in hot and cold water" by the manufacturer. Nevertheless, traces of PGPR are dissolving in water. To investigate factors influencing the dissolution of the surfactant in the aqueous phase PGPR was added to sunflower oil in concentrations of 1 or 10 wt%. Water samples of 70 ml were exposed to oil layers of 7 g. After 4 days the water phase was analyzed for its surface tension. A further water sample was exposed to pure sunflower oil, and the surface tension of pure water served as a reference.

In Fig. 4.6 the surface tensions of the water phase obtained from the different samples are plotted against time. A decrease in surface tension indicates transfer of surface active substances from the oil phase to the water. No difference was
observed between pure water and water exposed to sunflower oil. Therefore, the surface active molecules did not originate from the sunflower oil. Water exposed to oil containing PGPR displayed a strong decrease in surface tension. PGPR molecules or free fatty acids contained in PGPR appear to have migrated into the water, the stronger surface tension decrease of the 10 wt% PGPR sample indicating a concentration dependency for the extent of migration.

In a second approach the diffusion velocity of PGPR in pure water was investigated. For that purpose, an air bubble was formed in the tensiometer cuvette containing water. The bubble apex was situated 2 mm beneath the surface of the water. Surface tension of the water determined by the bubble shape is plotted against time in Fig. 4.7. For the first 15 min the water surface was left uncovered (closed symbols), subsequently it was covered by an oil layer containing 5 wt% of PGPR (open symbols). The surface tension of the water measured at the air bubble slightly decreased from 72 mN/m to 71 mN/m during the next 150 min. From that point on it dropped rapidly, indicating the adsorption of PGPR molecules at the bubble surface. The long period of 150 min for the small distance of only 2 mm implies a very low diffusion velocity of approximately 0.8 mm/h for PGPR in water.

Figure 4.6: Migration of surface active substances from oil to water phase. Surface tension of pure water and of water previously exposed to pure SFO, to SFO containing 1 wt% PGPR, or to SFO containing 10 wt% PGPR.
Figure 4.7: Migration of lipophilic surfactant PGPR from oil layer through 2 mm of water to the water-air surface. Decrease of surface tensions measured at the air bubble in the aqueous phase. First 15 min: no oil layer, pure water surface tension (closed symbols); 15 min to 230 min: addition of the oil layer, increasing turbidity of the oil, decreasing surface tension of the water (open symbols).

4.4 Transport processes across a thin oil membrane

4.4.1 Spontaneous emulsification

Spontaneous emulsification is a possible transport mechanism of water and substances dissolved therein across an oil layer. The spontaneous formation of emulsion droplets without shear or agitation energy was observed in the course of several experiments, visible as increasing turbidity of oil phases in contact with water. For instance in Fig. 4.7 spontaneous emulsification can be observed in the covering oil layer: transparent right after the addition (picture in the center) but turbid after 150 min (right picture).

The influence of emulsifier and electrolyte on the occurrence of such spontaneous emulsion droplet formation was studied at a simple oil/water interface using light microscopy. 2 ml of the aqueous phase in a petri dish were covered by an oil
Facilitated water transport across an oil membrane

layer of 7 ml. The inverse light microscope (Chapter 3.2.8) was focused on the interface and pictures were taken at regular intervals of 10 min. Fig. 4.8 shows light micrographs of the aged interface of several oil/water systems after 60 min at room temperature. From the top down the emulsifier concentration is increased. For both columns an increasing number of droplets was observed for higher amounts of PGPR. The addition of 5 wt% of salt (right column) had an inhibiting effect on the spontaneous emulsification. For all PGPR concentrations the samples containing salt in the aqueous phase displayed considerably less spontaneously generated droplets compared to samples containing pure water (left column). The emulsifier therefore benefits the spontaneous emulsification, while NaCl has an adverse effect. Similar findings were published by Greiner and Evans [86] who held the decreased osmotic pressure of the water responsible for the inhibition of the spontaneous emulsification.

4.4.2 Oil film thinning

To study the diffusion of water across an oil layer in a well defined system, model double emulsion drops were formed at the tip of a purpose-made double capillary. A small amount (about 1.7 µl) of sunflower oil containing PGPR was slowly inflated by approximately 60 µl of pure water resulting in an average oil layer thickness of 20 to 30 µm. The electrolyte, if any, was dissolved in the continuous phase. Caused by the osmotic gradient water diffusion from inner water phase through the oil film occurred and the drop volume continuously decreased. Driven by the buoyancy force the oil film started to accumulate at the drop apex. For some drops this resulted in an oil film rupture somewhere in the lower part of the drop. In other cases, the accumulation led to a local thinning of the oil layer, appearing as holes formed in the oil film (Fig. 4.9 picture (B)). Unless the drop burst, the thinned areas were expanding across the drop surface until a circular belt was formed (picture (C)). This band started to broaden until either the oil layer ruptured, or the inner aqueous phase was drained (pictures (D-E)).

Fig. 4.9 also shows the time dependence of the drop volume. The diffusion across the uniform oil layer was quite slow. To estimate the diffusion rate the first 600 data points for the drop volume, corresponding to a time interval of 100 min, were fitted using linear regression of type $y = ax + b$. The slope $a$ (equivalent to the volume flow rate in µl/min) was divided by the initial drop area $A_0(1)$ to obtain
Figure 4.8: Light microscopic pictures of spontaneous emulsification at an oil/water interface after 60 min of aging, water droplets formed in the oil phase. Oil phase containing 1 wt% (top), 5 wt% (middle), or 10 wt% (bottom) PGPR, water phase containing 5 wt% NaCl (right) or pure water (left).
the estimate of the diffusion rate.

From the time when first signs of film thinning appeared (Fig. 4.9 picture (B)) the diffusion rate strongly increased. For the estimation of the secondary diffusion rate appropriate data points (starting after the formation of the circular belt, picture (C) in Fig. 4.9) were chosen from the volume against time data set and fitted using a linear regression. In the majority of cases less data points were available for this range than for the uniform oil film due to rupture of the oil layer. Because of the inhomogeneous distribution of the oil and the fast change in drop volume and surface it proved to be more difficult to determine the zero drop area $A_0$ relevant for this secondary diffusion. To enable the comparison of the individual results $A_0(2)$ was chosen to be the area of the drop at the intersection point between the two linear fits (Fig 4.10).

PGPR concentrations of 0, 1, and 5 wt% in the oil film were combined with electrolyte concentrations of 2 and 5 wt% in the outer aqueous phase. The film thinning appeared for all investigated combinations except for the samples without PGPR. These samples showed film rupture for all examined drops. Samples containing 1 or 5 wt% PGPR developed the film thinning phenomenon in most cases, at least to some extent. Therefore, the assumption was made that the thinned film is stabilized by PGPR. We assume that the film consists of PGPR bi- or multilayers, with the sunflower oil almost completely drained in direction of the drop apex.

Starting time of the film thinning was defined as the moment the first 'hole' in the oil layer was observable. No correlation between drop composition and this film thinning starting time could be observed. Even for samples identical in composition, drop size, and film thickness it varied by up to factor of ten.

### 4.4.3 Diffusion across the intact oil layer

The diffusion rate of water across a thick oil layer, i.e. the intact oil film previous to the film thinning, is plotted against surfactant concentration in Fig. 4.11. For each electrolyte/surfactant-combination four droplets were evaluated except for the 2 wt% NaCl / 5 wt% PGPR sample, where due to early film thinning only two measurements could be included.

The diffusion across a pure sunflower oil layer turned out to be faster than for the samples containing PGPR, but considerably less reproducible. Presumably
4.4 Transport processes across a thin oil membrane

Figure 4.9: Double emulsion model droplet containing pure water in the inner aqueous phase, 2 wt% of NaCl in the outer aqueous phase, and 5 wt% of PGPR in the oil film. Decrease of the drop volume due to water diffusion. Droplet with intact oil film causing slow diffusion (A), onset of local film thinning ('hole formation') leading to increased diffusion (B), circular band formation of the thinned area (C), broadening of thinned area and fast decrease of the drop volume (D, E). Drop volume is plotted against time, the gray parts of the curve were fitted using linear regression \( y = ax + b \) to determine the diffusion rate.
some surface active ingredients of the sunflower oil support water diffusion, these ingredients being displaced from the interface by the addition of PGPR.

In contrast to publications claiming that increased lipophilic emulsifier content leads to an increased transport rate [46, 73, 88–90], no difference was observed between PGPR concentrations of 1 wt% and 5 wt%. These two concentrations showed a very similar interfacial tension (Fig. 4.3) indicating a concentration range > CMC. Possibly this high PGPR concentration leading to high amounts of excess PGPR after the covering of both, internal and external interface, was responsible for the lack of increase in transport rate. In literature a decrease in transport rate is mentioned if a certain surfactant concentration is exceeded [8, 73]. This decrease was explained by the increasing oil phase viscosity, an explanation not applicable to the present PGPR/SFO system.

Wen and Papadopoulos [74] claimed that the salt concentration in the case of non contacting droplets (i.e. for high oil film thickness) had little or no effect on water transport rate. The results displayed in Fig. 4.11 do not support these findings. The authors also claim, that reverse micellisation and spontaneous emulsification is responsible for the transport across broader oil films. Observations made in the model drops support this theory, since increasing turbidity was observed in the oil layer. Spontaneous emulsification is inhibited by increasing salt...
4.4 Transport processes across a thin oil membrane

Figure 4.11: Water diffusion across an intact oil film containing different amounts of PGPR in the sunflower oil driven by NaCl concentrations of 2 wt% (open symbols) or 5 wt% (closed symbols) in the outer aqueous phase.

concentration (see Chapter 4.4.1). This fact supports the findings of an NaCl-dependent diffusion rate as shown in Fig. 4.11. If spontaneous drop formation occurs at the inner water/oil interface and is increasingly hindered by NaCl at the outer oil/water interface, transport in direction of the outer aqueous phase will occur and be strongly influenced by the electrolyte. Florence and Whitehill [1] observed an influence of the electrolyte not only on the osmotic pressure but also on the rigidity of the interfacial layer, thus hindering water transfer. Nevertheless, the change in transport rate reported in Fig. 4.11 is attributed solely to the osmotic gradient. An influence of the interfacial film rigidity is ruled out due to the findings in Chapter 4.3.2 where no influence of NaCl on the interfacial elasticity was observed.

4.4.4 Diffusion across a thin film

For the diffusion rate across the thin film less data points are available. Some model drops displayed no film thinning at all, and many persisted not long enough for the diffusion rate to be reliably evaluated. In accordance with the findings of Wen and Papadopoulos [80] for droplets in visual contact (i.e. very thin oil layers), the transport rate increased for increasing electrolyte concentration i.e. for
increasing osmotic gradient. In Fig. 4.12 samples for both PGPR concentrations display higher diffusion rates for higher NaCl concentrations. Therefore the diffusion across the thin film is also driven and influenced by the osmotic gradient.

Higher surfactant contents again did not increase the transport rate. Quite the contrary, a reduced diffusion rate for higher PGPR concentrations was observed for both electrolyte concentrations.

Figure 4.12: Water diffusion across a thinned oil film containing different amounts of PGPR in the sunflower oil driven by NaCl concentrations of 2\% (open symbols) or 5\% (closed symbols) in the outer aqueous phase.

Transport rates across the thin film were at least 40 times higher than the rates for water transport across the intact oil layer. This factor may be even higher, given the fact that the entire drop surface \( A_0 \) was used in the calculation of the the transport rate, and not the smaller drop surface part where the thinning and with it the transfer actually occurred. The magnitude of the increase indicates different transport mechanisms for the two situations. Wen and Papadopoulos [80] observed similar trends for the transport of water from single globules: if the globule was in visual contact with the O/W interface, the transport rate was increased by a factor of 20. They claimed that in the visual contacting case water transport occurred through hydrated surfactant mechanism (see Chapter 2.2.2), else by inverse micellation and spontaneous emulsification [81].

The above results support the assumption of reverse micellation and spontaneous emulsification as mechanism for the transport across an intact, 'thick' oil layer.
Nevertheless, for thin oil films the hydrated surfactant mechanism should lead to an increasing transport rate for increasing surfactant concentration [80]. Therefore, for the diffusion across thin film in the double emulsion model droplet we propose the ‘passage through thin surfactant lamellae’ [44, 48, 72, 78] mechanism. An increased surfactant content might lead to more densely packed surfactant layers or even to multilayers at the interface. These structures potentially hinder the transport, leading to a lower diffusion rate for higher surfactant contents.

4.5 Conclusions

In order to obtain a better understanding of factors influencing multiple emulsion stability and processes participating in the swelling-breakdown of W/O/W systems, properties of the interface and incidents affecting the interface were investigated.

The interfacial tension between sunflower oil and water was measured using tensiometry. The addition of 1% PGPR to the oil phase strongly decreased the interfacial tension. Further addition of PGPR did not result in a further reduction. This was attributed to the occupation of the entire droplet interface already for small PGPR concentrations. The only impact of higher surfactant concentrations was a faster decrease and more rapid achievement of the equilibrium interfacial tension. Further decrease of the interfacial tension was possible at all surfactant concentrations by the addition of electrolyte. NaCl contents of up to 10% were investigated and found to have a systematically decreasing effect on the interfacial tension. The lyotropic salt NaCl is known to reduce the solubility between nonionic surfactant and the aqueous phase, leading to increased adsorption of the surfactant at the interface.

The interfacial elasticity measured by oscillatory tensiometry was expressed by the interfacial dilatational modulus |E*|. In contrast to the interfacial tension, the interfacial elasticity was not influenced by the addition of electrolyte. Increasing amounts of PGPR, however, led to a decrease in dilatational modulus and therefore to a decrease in surface elasticity. We assume that surface active substances present in sunflower oil tend to form a network structure. The displacement of these substances from the interface by increasing amounts of PGPR is suspected to be the reason for the decreasing elasticity. Therefore the superior stability of multiple emulsion containing high amounts of PGPR was not due to a rigid film formed by the surfactant.
The lipophilic surfactant PGPR was found to migrate to the aqueous phase in small amounts. Water previously exposed to sunflower oil containing PGPR displayed a decreased surface tension, while pure sunflower oil had no such effect. Nevertheless the diffusion velocity of the surfactant in water was very low.

During interfacial tension measurement an increasing turbidity of the oil phase close to the interface was observed. This turbidity was investigated using light microscopy and identified to be caused by spontaneous emulsification. The spontaneous formation of water droplets in the oil phase was strongly promoted by increasing PGPR concentrations. The addition of NaCl, however, displayed an inhibiting effect on the droplet formation. The reason for the inhibition is assumed to be the decreasing osmotic pressure of the water.

To study the diffusion of water across an oil layer in a well defined system, model double emulsion droplets were formed at a purpose-made double capillary. Water diffusion from the inner water phase across the oil layer was generated by electrolyte in the outer aqueous phase, the transport rate was determined by the decrease in drop volume. Driven by buoyancy force the oil film started to accumulate at the drop apex, sometimes resulting in an oil film rupture. In other cases, the accumulation led to a local thinning of the oil layer. Unless the drop burst, the thinned areas were expanding across the drop surface until a circular belt was formed. This band started to broaden until either the oil layer ruptured, or the inner aqueous phase was drained.

Water transport across the intact oil layer occurred at a slow diffusion rate of around 0.01 µl h⁻¹ mm⁻². Higher osmotic gradients led to faster transport, whereas an increased PGPR content had no influence on the diffusion. The transport across the oil layer of approximately 25 µm thickness was attributed to reverse micellisation and spontaneous emulsification.

At the time the film thinning occurred, the diffusion rate increased strongly, reaching high values of about 0.4 µl h⁻¹ mm⁻². Higher electrolyte concentrations still caused increased diffusion rates. High surfactant concentrations, however, led to a decrease in water transport. The transport mechanism of hydrated surfactants would in this case lead to an increased transport rate, therefore passage through thin surfactant lamellae was proposed to be responsible for water transport.
5 Conclusions

Within the scope of the present work the particular suitability of the rotating membrane (ROME) device for the production of multiple emulsions was shown. A multiple emulsions system of W/O/W type with promising applications for example in food or cosmetics industry was investigated. The swelling-breakdown process leading to its formation was analyzed using two different rheological approaches. The influence of various ingredients and process parameters on the process and the final product was observed. Due to the superposition of many actions it was difficult to conclusively deduce the principles of the process from the multiple emulsion system. Thus, properties of the oil/water interface and incidents affecting the interface were investigated using different tensiometric methods. Furthermore a model double emulsion droplet with well-defined properties was formed at a double capillary to study osmotic pressure gradient induced transport processes across the oil layer.

The first part of this work (Chapter 3) focuses on the production of multiple emulsions and on the osmotic gradient induced swelling-breakdown process within the multiple emulsion system. The gentleness of the ROME device was evidenced by investigating the loss of inner aqueous phase during the production of a multiple emulsion. Compared to a continuous rotor/stator process the rotating membrane apparatus proved to be clearly superior for the fabrication of more delicate multiple emulsion systems yielding large internal water phase fractions. The system containing a small share of enclosed aqueous phase was successfully produced by both devices with hardly any leakage detected.

Highly viscous emulsions containing low amounts of fat are of considerable interest for cosmetic or food industries. Such systems were produced by taking advantage of the so-called 'emulsion swelling process', the transport of water from outer to inner aqueous phase induced by an osmotic gradient. Swelling of emulsions is always accompanied by breakdown, leading to the release of inner aqueous phase and substances encapsulated therein. Two different rheological methods were applied to monitor the combined swelling-breakdown process: yield stress
5 Conclusions

determination and oscillatory rheology. Both methods were suitable to follow the process, although oscillatory rheology provided more structure information and resulted in a better resolution for short time tests.

Two main parameters showed significant impact on the swelling-breakdown behavior of the investigated system: the electrolyte (sodium chloride, NaCl) and the lipophilic surfactant (polyglycerol polyricinoleate, PGPR). Two main functions of the lipophilic surfactant were identified: the stabilization of new interface generated by growing internal water droplets, and the protection of the inner aqueous phase during the secondary emulsification step in order to avoid losses at this stage. For very low surfactant concentrations, almost no emulsion swelling was observable.

The electrolyte also showed a minor impact on the magnitude of the swelling. Reason is a stabilization of inner droplets during the secondary emulsification step by the electrolyte, and thus reduced leakage at this stage. In contrast, the diffusion rate was mainly controlled by the salt, the achievement of a maximum viscosity was delayed by a decrease in salt content. The earlier appearance of the peak viscosity for low surfactant concentrations, however, was not the result of a change in diffusion rate but rather of an earlier superposition of the swelling by breakdown. We assume that water transport occurs mainly by a mechanism that does not require high amounts of free surfactants.

The major difficulty arising from the study of transport processes in multiple emulsion systems is the superposition of swelling and breakdown, making it impossible to investigate the influence of one single parameter on the diffusion process. To obtain a better understanding of these parameters, the oil/water interface and processes affecting this interface were studied in the second part of this work (Chapter 4).

Interfacial tension between sunflower oil and water was strongly decreased by small amounts of PGPR in the oil phase, whereas a further addition of PGPR did not result in a further reduction. Nevertheless, it was possible to additionally decrease the interfacial tension by the addition of the lyotropic electrolyte NaCl which is known to lead to increased adsorption of nonionic surfactants at the interface. Interfacial elasticity, however, was not influenced by the electrolyte. PGPR led to a decrease in interfacial elasticity due to displacement of surface active substances present in sunflower oil which are more inclined to the formation of a network structure.

Spontaneous emulsification, appearing at oil/water interfaces of systems containing PGPR, was identified as a mechanism for water transport. The occurrence of
spontaneous emulsification, i.e. the formation of water droplets in the oil phase, was strongly promoted by increasing surfactant concentration, whereas the addition of electrolyte displayed an inhibiting effect. The inhibition is assumed to be caused by the decreasing osmotic pressure of the aqueous phase.

Water diffusion across an oil layer was studied in well-defined model double emulsion droplets formed at a purpose-made double capillary. Two different situations had to be considered: diffusion across an intact oil layer of about 25 µm and diffusion across a thinned area expanding from the capillary towards the drop apex until either the oil layer ruptured or the inner aqueous phase was drained. The occurrence of film thinning, even if only a small 'hole' in the interface was observable, led to an increase in diffusion rate of more than an order of magnitude. The thinned film is assumed to consist of a surfactant bilayer or a few surfactant layers, with the entire sunflower oil drained from in between. We conclude that different transport mechanisms are responsible for the increase. The first was identified as spontaneous emulsification and reverse micellation, respectively. A second transport mechanism, passage through thin surfactant lamellae, is proposed to be responsible for the increased water transport across a thin oil film.

For both cases, intact and thinned oil film, increased osmotic gradients led to faster diffusion. For the intact oil layer no influence of the surfactant on the transport rate was observed, whereas an increased surfactant content led to reduced water transport across the thinned film.
Bibliography


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Curriculum Vitae

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