Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

On the pressure balance and the resulting phase fraction in compressed multiple emulsions

Sebastian Beer [a,b,*], Dorota Dobler [a], Thomas Schmidts [a], Michael Keusgen [b], Frank Runkel [a,c]

[a] Technische Hochschule Mittelhessen, Wiesenstraße 14, 35390 Gießen, Germany
[b] Philipps-Universität Marburg, Biegenstraße 10, 35037 Marburg, Germany
[c] Justus-Liebig-Universität Gießen, Ludwigstraße 23, 35390 Gießen, Germany

HIGHLIGHTS

- The relationship between phase fractions and pressure gradients in multiple emulsions is quantified.
- A method to determine the disperse phase fraction is developed and presented.
- Based on the measured disperse phase fraction, the encapsulation efficiency is determined.
- The formation of compressed multiple emulsion during production is analysed.

GRAPHICAL ABSTRACT
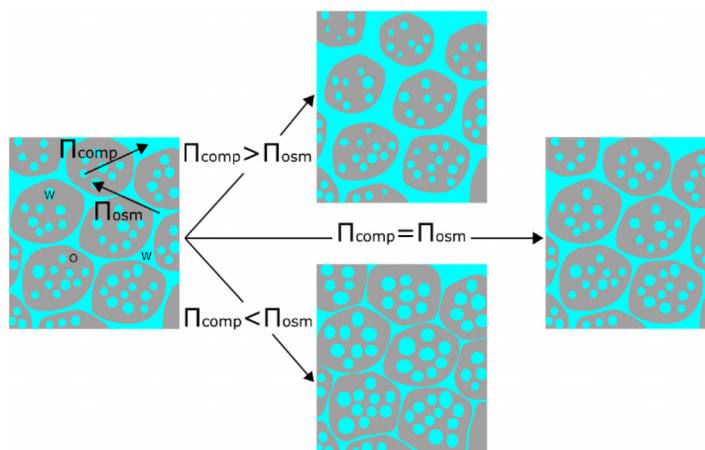
ARTICLE INFO

ABSTRACT

While swelling and shrinking of multiple emulsions – depending on existing pressure gradients – has been well reported in the literature, little research has been carried out covering the osmotic equilibration between pressure systems caused by interfacial phenomena and phase fractions for multiple emulsions in which either one or both disperse phases exhibit a phase fraction above the maximum packing limit without any deformation of the droplets. In this paper, a model for determining the theoretical equilibrium state regarding osmotic regulation is presented, as well as a new experimental method to determine the disperse phase fraction. This method is employed to compare the measured phase fractions to the theoretical predictions. Using both experimental and theoretical approaches, a direct method is proposed to define the disperse phase fraction and the encapsulation efficiency, yielding potential for a knowledge driven improvement of the production of multiple emulsions.

© 2016 Elsevier B.V. All rights reserved.

* Corresponding author at: Technische Hochschule Mittelhessen, Wiesenstraße 14, 35390 Gießen, Germany.
  E-mail address: Sebastian.Beer@lse.thm.de (S. Beer).

Symbols

Φ	disperse volume fraction
Φ_{max}	maximum disperse volume fraction without deformation of droplets
$\Phi_{W/O/W}$	disperse volume fraction of the multiple droplets with regard to the total volume of the emulsion
$\Phi_{W/O}$	disperse volume fraction of the water droplets with regard to the multiple droplets
Φ_{Wo}	volume fraction of the continuous water phase
Φ_{Wi}	volume fraction of the disperse water phase
Φ_O	volume fraction of the oil phase
c_i	osmotic concentration in the disperse water phase
c_o	osmotic concentration in the continuous water phase
n_i	amount of osmotic entities in the disperse water phase
n_o	amount of osmotic entities in the continuous water phase
V_0	volume of the subject emulsion
$r_{32W/O}$	sauter mean radius of the disperse water droplets
$r_{32W/O/W}$	sauter mean radius of the multiple droplets
$\sigma_{W/O}$	interfacial tension of the water-in-oil interface
$\sigma_{O/W}$	interfacial tension of the oil-in-water interface
$\Pi_{Laplace}$	Laplace pressure
Π_{osm}	osmotic pressure caused by differences in osmotic concentration
Π_c	osmotic pressure caused by deformation of droplets
DPF	disperse phase fraction
EE	encapsulation efficiency

1. Introduction

After the first description of multiple emulsions 90 years ago, a wide field of potential applications has been proposed [1]. Multiple emulsions were suggested for use in the pharmaceutical, cosmetic and food technology [2,3]. The wide application of multiple emulsions in these fields yet has to leave the state of theoretical considerations; the widespread use of multiple emulsions has not taken place until today. The main reason for this situation is the fact, that the apparently simple mixture of water, oil and two emulsifiers creates a complex system expressing various effects which hinder a controlled, reproducible production and might lead to destabilisation. Some of these effects appear in simple emulsions (including flocculation, sedimentation, coalescence, Ostwald ripening), while others are specific for multiple emulsions (swelling/shrinking, migration of emulsifiers, droplet breakup). Here we propose a theoretical model describing the relationship between the pressure systems in multiple emulsions and the disperse phase fraction (DPF), leading to a deeper understanding and therefore to a better control of the production process of multiple emulsions.

While the counteraction of the Laplace pressure by an osmotic pressure is common [4] (and has been extensively analysed regarding the morphology of the emulsion droplets by Mezzenga et al. [5]), little research has been published describing the pressure systems caused by interfacial phenomena in compressed multiple emulsions; an emulsion where either the primary phase or the multiple phase or both have a DPF Φ over its maximum packing limit without any significant deformation Φ_{max}. The compressed packing at $\Phi > \Phi_{max}$ results in deformation of the droplets from their spherical form to a rather polyhedragonal form; thereby increasing the interfacial area and thus increasing the pressure in the disperse phases (also referred to as osmotic pressure). The relationship between the compression and the increase in the osmotic

pressure was initially described by Princen and Kiss for a simple polydisperse emulsion [6]. Considering compressed multiple emulsions, the osmotic pressure becomes a crucial parameter, as multiple emulsions can undergo swelling or shrinking following an existent pressure gradient, thereby altering the desired DPF [7]. The DPF is an important aspect of compressed emulsions, as it is directly related to the rheological parameters of the emulsion; thereby affecting the final emulsion as well as the production parameters [8]. The osmotic pressure caused by the compression of the emulsion can be counteracted by the addition osmolytes into the inner phase.

In this paper, a compressed multiple water-in-oil-in-water (W/O/W) emulsion with an initial disperse phase fraction of 0.8 in the primary and the multiple emulsion is presented. Considerations concerning the theoretical pressure balance regarding osmotic regulation are presented as well as a localised fluorescence microspectroscopic method to determine the true phase fraction and thereby gaining insight into the pressure system of the presented emulsion.

2. Theory

2.1. Pressure balance in compressed multiple emulsions

For multiple emulsions of the non-compressed type it is necessary to add osmolytes to the inner disperse water phase to counteract the Laplace pressure

$$\Pi_{Laplace} = \frac{2\sigma}{r_{32}} \tag{1}$$

with σ being the interfacial tension of the respective interface and r_{32} being the sauter mean radius of the droplets. The sum of the Laplace pressure of the inner and multiple droplets has to be equilibrated using a higher osmotic concentration in the inner water phase to avoid shrinking – a water flow from the inner to the outer waterphase – of the multiple emulsion.

$$\Pi_{osm} = \Delta cRT \tag{2}$$

with Δc being the difference of concentration of osmotic active entities across the oil barrier, R being the gas constant and T being the absolute temperature.

Increasing the DPF above Φ_{max}, the osmotic pressure adds to the overall pressure. Maestro et al. have provided a model which proved to be valid for a wide range of droplet sizes and polydispersities:

$$\Pi_c = k \frac{(\Phi - \Phi_{max})^2}{\sqrt{1-\Phi}} \frac{\sigma}{r_{32}} \tag{3}$$

with the parameters $k = 3.2$ and $\Phi_{max} = 0.64$ for polydisperse emulsions [9] (to avoid confusion the osmotic pressure caused by the compression of the emulsion is depicted as Π_c). Combining the pressure systems for the primary and the multiple emulsion yields the total pressure

$$\Pi_{total} = \Pi_{Laplace\,W/O} + \Pi_{Laplace\,O/W} + \Pi_{c\,W/O} + \Pi_{c\,O/W} \tag{4}$$

The total pressure has to be counterbalanced using a difference in osmotic concentration obtained from Eq. (2).

2.2. Applicability of the described model to experiments

Considering the experimental realisation, some aspects appear, hindering an exclusively theory based experimental design: when applying the common two-step procedure reported by Matsumoto et al. [10], apart from the polydispersities produced, other aspects have to be considered. Due to the rather rough method of homogenising the primary emulsion in the outer water phase,