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# $W_1/O/W_2$ double emulsions stabilised by fat crystals – Formulation, stability and salt release

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ABSTRACT

Water/oil ($W_1/O$) emulsions containing fat crystals have been incorporated into an aqueous phase containing 1% na-caseinate as emulsifier to create stable water/oil/water ($W_1/O/W_2$) double emulsions. The $W_1/O$ primary emulsion was stabilised exclusively with monoglyceride and triglyceride crystal "shells", and contained 30% $W_1$ aqueous phase as well as KCl.

The stability of the double emulsions was monitored over the course of 6 weeks. It was found that, providing some salt or sugar were present in the $W_2$ aqueous phase, emulsions retained their double structure – although coalescence between double emulsion globules occurred and creaming was observed. KCl encapsulated in the $W_1$ phase of the primary emulsion was only slowly released to the $W_2$ continuous aqueous phase: 20% within 6 weeks. This release is due to the damage caused to the fat crystal shells during the secondary emulsification step used to create the double emulsion structure.



## 1. Introduction

Double emulsions have long been seen as having a great potential in many industrial sectors, such as the pharmaceutical, agricultural, and especially the food industry. Although numerous applications can be envisaged, these systems are especially of interest in the creation of low-fat foods such as mayonnaise, soups and salad dressings. Current low fat food technologies rely on replacing some of the oil phase with water-soluble ingredients, such as biopolymers, that increase the viscosity of the emulsion's aqueous phase. Although such an approach does lead to the reduction of oil content, the physical and organoleptic properties can be significantly affected and thus the incorporation of these into food can lead to an inferior product in terms of mouthfeel and flavour [1].

An alternative approach to reducing the effective oil content of an emulsion, while retaining its sensory properties, is to incorporate water droplets into the oil phase – i.e. replace the oil with a water-in-oil (W/O) emulsion. This creates a $W_1/O/W_2$ double emulsion, and, depending on the volume fraction of the inner $W_1$ aqueous phase, a potentially large amount of oil can be replaced this way. The benefit of this approach is that the oil phase potentially appears unchanged to the consumer and thus sensory properties should remain similar to those of a full fat product. In order to achieve this, care should be taken to ensure that the oil droplets (containing the primary emulsion) in the double structure and those in the simple emulsion are of very similar sizes.

However, the most common problem associated with double emulsions is their inherent thermodynamic instability. The existence of two oppositely-curved interfaces within the same structure requires two different emulsifiers (one lipophilic, one hydrophilic) to stabilise the double emulsion. The two emulsifier species have a tendency to diffuse from one interface to the other, which changes the curvatures of both and subsequently destabilises the structure to give simple O/W emulsions. This is especially so when small-molecule emulsifiers are used, as these have a higher mobility than large molecules such as proteins [2–5]. Double emulsions therefore tend to be more stable if the surfactants have a large molecular size, as this "anchors" them to the respective interface (the energy required to remove large molecules from an interface is high) and makes them less likely to diffuse between interfaces [3,6]. Another factor affecting the stability of double emulsions is the existence of osmotic pressure gradients. A difference in the osmotic pressure between the two aqueous phases either causes water from the external $W_2$ phase to be transported to the internal $W_1$ phase or vice versa, depending on the direction of the gradient. In the first case, the internal $W_1$ droplets swell due to the increased phase volume of encapsulated water, while in the latter case, $W_1$ droplets gradually empty. In both cases, the double emulsion structure is gradually converted to a simple O/W emulsion [7–10].

In food-grade double emulsions, where the choice of surfactants is limited to tightly regulated food-grade ingredients, PGPR (polyglycerol of polyricinooleates) is often used as the emulsifier for the primary W/O emulsion [11,12]. However, the use of PGPR in food-grade applications is currently very limited and in addition it can result in a bitter flavour, especially noticeable at higher

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concentrations. Furthermore, it cannot prevent leakage of an encapsulated solute from the $W_1$ phase to the continuous $W_2$ phase unless the osmotic pressure between the two aqueous phases is matched.

In the present study we have investigated double emulsions where stabilisation of the primary W/O emulsion was achieved using fat crystals, while the second surfactant was sodium (na-) caseinate. Particles have been known for over a century now to be excellent stabilisers to emulsions [13]. Fat crystals have been shown to impart good stability on W/O emulsions by forming sintered "shells" around the water droplets [14], hence providing a special form of Pickering stabilisation. However, the existence of fat crystals in a dispersed oil phase is usually a source of instability to O/W emulsions [15]. If the crystals protrude from the droplet surface they may "pierce" neighbouring droplets, which causes aggregation and eventual coalescence between two (or more) oil droplets since fat crystals are preferentially wetted by the oil phase.

However, it is demonstrated that by controlling the fat crystal concentration, fat-crystal stabilised $W_1/O$ emulsions can be incorporated into a double emulsion structure. Furthermore, it is shown that these double emulsions are able to resist osmotic pressure gradients and can effectively retain an encapsulated solute within the primary emulsion droplets.

## 2. Experimental

### 2.1. Materials

Distilled water and commercially available sunflower oil were used as the water and oil phases, respectively, of all prepared emulsions. Distilled saturated monoglycerides (MG), an equal mixture of Dimodan HP and Dimodan P Pel/B, and spray-dried sodium caseinate were obtained from Danisco, UK. PGPR (Palsgaard 4150) was supplied by Palsgaard, Denmark. Glycerin Tripalmitate (tripalmitin), D-(+)-glucose, potassium chloride, sodium chloride and sodium azide were all obtained from Sigma, UK. All materials were used as received, without further purification. All percentages of the water and oil phases listed below are weight/total weight of the emulsion. The percentages of the components in the oil or water phase are given as percentage weight per total weight of the oil or water phase, respectively.

### 2.2. Methods

#### 2.2.1. Primary emulsion preparation

($W_1/O$) all primary water-in-oil ($W_1/O$) emulsions were formulated using a 30% aqueous phase ($W_1$), containing 1.6% KCl and 0.01% Na-azide, and a 70% oil phase (O), which included 1.25% saturated monoglyceride and 2.5% tripalmitin. The choice of the mono-and triglyceride concentrations was based on previous experiments showing that this ratio of crystallising material to oil resulted in stable emulsions. All primary emulsions were then prepared using the process described previously [14].

For comparison, a simple 30% W/O emulsion, containing solely PGPR as the emulsifier component, was also prepared, by mixing 30% water (containing 1.6% KCl) with 69% sunflower oil and 1% PGPR and subsequently shearing the system for 5 min using a Silverson High Shear mixer.

Finally, in one formulation 1% PGPR was added to the prepared primary emulsion containing fat crystals and dispersed by gentle agitation, in order to investigate the influence of PGPR on the emulsion containing fat crystals.

#### 2.2.2. Double emulsion preparation ($W_1/O/W_2$)

In order to obtain double emulsions, sunflower oil was mixed with the $W_1/O$ primary emulsion in a ratio of 1:1, thus reducing the $W_1$ water content to 15%, before 20 g of this blend was slowly mixed with 80 g of the continuous $W_2$ aqueous phase. The $W_2$ phase contained 1% sodium caseinate which was dissolved in distilled water, and also a small (0.01%) amount of sodium azide to prevent microbial contamination. Varying concentrations of glucose (4–16%), or NaCl (1–5%) were added to the $W_2$ aqueous phase in order to create various osmotic pressure gradients ($\Delta\pi$) between encapsulated ($W_1$) and continuous aqueous phase ($W_2$) (see Table 1). The osmotic pressure gradient between the aqueous phases was calculated based on the difference in the molar concentration of the solutes in the two phases.

The formulation was subsequently sheared at 8000 rpm for 3 min using a Rotor/Stator apparatus (Silverson), while being placed in an ice bath to avoid an increase in temperature in the sample, which could melt the crystal network surrounding the $W_1$ primary emulsion droplets.

#### 2.2.3. Emulsion droplet size measurement and microstructure visualisation

The droplet sizes in the primary emulsions prior to incorporation within the double structure were measured using a nuclear magnetic resonance (NMR) device (Bruker Minispec NMR, Bruker Optics, UK), equipped with a gradient unit as previously detailed [14]. Measurements were performed on three different samples.

Light microscopy (Reichert Jung Polyvar) was used to visualise the double emulsion droplets and to determine the size of the primary emulsion droplets (post incorporation into the double structure) and that of the double emulsion globules. Image analysis software (ImageJ) was used to obtain size distribution data from the obtained micrographs of the double systems. In order to obtain an accurate measure of the size distribution of the double emulsion globules and the $W_1$ primary emulsion droplets, at least 2–3 different samples of each formulation were characterised by counting 500–1000 droplets in each case. The standard deviation ($\sigma$) from the mean droplet size is also given as it provides an indication of the breadth of droplet size distribution (i.e. a small $\sigma$ value indicates a narrow size distribution).

Cryo-SEM (Philips XL-30 FEG ESEM) was used to visualise the double emulsion microstructure. Samples were shock-frozen in liquid nitrogen, and dusted with gold particles prior to analysis in the SEM.

#### 2.2.4. Conductivity measurements

In order to determine the effectiveness of the double emulsion structures in retaining a solute (KCl in this case) within the inner

**Table 1**
Directions of osmotic pressure gradients: a positive $\Delta\pi$ indicates the concentration of solute is greater in $W_1$ than in the continuous $W_2$ aqueous phase.

| Osmotic pressure gradient, $\Delta\pi$ (atm) | Molar concentration of solute | Concentration (NaCl) in $W_2$ (%) | Concentration (glucose) in $W_2$ (%) | Preferential transport of water |
|---|---|---|---|---|
| 11 | $W_1 > W_2$ | 0 | 0 | Into droplets |
| 5.5 | $W_1 > W_2$ | 1.3 | 4 | Into droplets |
| 0 | $W_1 = W_2$ | 2.6 | 8 | None |
| −11 | $W_2 > W_1$ | 5.2 | 16 | Out of droplets |