Food Hydrocolloids 42 (2014) 215–222

Contents lists available at ScienceDirect

Food Hydrocolloids

journal homepage: www.elsevier.com/locate/foodhyd

Comparative study of the stability of multiple emulsions containing a gelled or aqueous internal phase

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ARTICLE INFO

Article history:
Received 18 February 2014
Accepted 27 May 2014
Available online 5 June 2014

Keywords:
Multiple emulsion
Stability
Food
Gel
Polymer

ABSTRACT

Water in Oil in Water (WOW) multiple emulsions have, for many years, been studied in order to utilise their functionality in food and pharmaceuticals, for reduced fat formulation, drug delivery and taste masking applications. However, their complex structure is susceptible to a broader range of instabilities than conventional emulsions. In this study we investigate the role of different emulsifiers and a simple, novel approach to gel the internal aqueous droplets to improve the stability to heat, shear, and the presence of salt. Changes in salt concentration can be detrimental to multiple emulsions, as this will induce swelling or shrinkage of the internal water droplets. Polyglycerolpolyricinoleate (PGPR) was the preferred low HLB emulsifier, and its presence dominated the stability of the WOW emulsions, irrespective of the high HLB emulsifier. However, lecithin was found to be the most stable high HLB emulsifier to heating. Gelling the internal water droplets with either alginate or carrageenan reduced the size of the water droplets, probably due to reduced recoalescence rates. The multiple Gel in Oil in Water (GOW) emulsions were more stable to the addition of up to 1 wt% salt to the external phase than WOW emulsions. In addition, the presence of xanthan in the external phase further improved the stability to the addition of salt. Therefore GOW emulsions show potential to be used in a realistic food processing environment, showing stability to shear, temperature and changes in salt concentration.

1. Introduction

There has been a long standing interest in developing multiple emulsions in food (Dickinson, 2011; Dickinson, Evison, & Owusu, 1991; Matsumoto, 1986) and pharmaceutical applications (Davis & Walker, 1987; Degim & Celebi, 2007). The interest stems from their unique structure, in that for Water-in-Oil-in-Water (WOW) emulsions, the dispersed oil droplets themselves contain aqueous phase droplets which can be used to carry guest molecules or simply contribute to the overall dispersed phase volume. WOW emulsions have been the main focus of research, particularly for food applications, and have been studied because of their added functionality in terms of reducing fat content in foods (Lobato-Calleros, Recillas-Mota, Espinosa-Solares, Alvarez-Ramirez, & Vernon-Carter, 2009; Lobato-Calleros et al., 2008), encapsulation of volatiles(Dickinson, Evison, Gramshaw, & Schwope, 1994), delivering bioactive compounds (Owusu, Zhu, & Dickinson, 1992), and taste masking of drugs and other compounds (Sonawane, Maria, Shinde, Hawaldar, & Pawar, 2010; Vaziri & Warburton, 1994). Although they have great potential in these applications, the biggest barrier to their use is their poor stability (Dickinson, 2011) which arises from the presence of the internal water droplets. In the preparation of double emulsions 2 types of emulsifiers are required, firstly a lipophilic emulsifier with a low Hydrophile–Lipophile Balance (low HLB) emulsifier soluble in the oil phase is required to stabilise the primary, internal water-in-oil (WO) emulsion droplets, and secondly, a hydrophilic (high HLB) emulsifier is needed in the external aqueous phase to stabilise the secondary oil droplets. The primary water droplets require a low HLB emulsifier, and are sensitive to coalescence both with other droplets, but also with the outer continuous phase (Dickinson, 2011; Dickinson et al., 1994), thus losing the whole basis of their added functionality. WOW emulsions can also lose water to the outer phase through mass transport driven by osmotic and chemical potential differences between the inner and outer water phases (Dickinson, 2011; Pawlik, Cox, & Norton, 2010). Because of the specific physical requirements of the low HLB emulsifier to stabilise the water droplets, it is beneficial for the emulsifier to possess a large, steric hydrophobic group, however, only a limited number of

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http://dx.doi.org/10.1016/j.foodhyd.2014.05.023
0268-005X/

food approved emulsifiers are suitable. From the various emulsifiers tested, only a few showed any WO stabilising properties, and only polyglycerolpolyricinoleate (PGPR) imparted significant stability to the WO emulsions over a range of conditions, agreeing with other studies of WO emulsion stability (Ushikubo & Cunha, 2014).

The second stage of multiple emulsion formation is the emulsification of the WO emulsion into the continuous aqueous phase. This requires a high HLB emulsifier to provide a stabilising layer around the oil droplets. The functionality of these emulsifiers is the same as for stabilising conventional oil in water (OW) emulsions. Commonly used high HLB emulsifiers include proteins such as caseins and whey proteins, or hydrophilic low molecular weight emulsifiers such as polysorbates and lecithins.

The more complex structure of WOW emulsions means that their kinetic stability is limited (Sapei, Naqvi, & Rousseau, 2012) as well as changes in morphology. Different approaches have been used to solve these stability issues, including careful choice of emulsifiers (Akhtar & Dickinson, 2001) and the use of steric stabilizers, fat crystals and protein-polysaccharide mixtures (Sapei et al., 2012). Several studies have shown that incorporating a polymer or protein in the internal water droplets, perhaps to gel the internal water droplets, thus forming a gel-in-oil-in-water (GOW) emulsion, can improve stability (Benichou, Aserin, & Garti, 2004; Dickinson, 2011). These include proteins such as sodium caseinate, whey protein and gelatin (Hemar, Cheng, Oliver, Sanguansri, & Augustin, 2010; Su, Flanagan, Hemar, & Singh, 2006; Surh, Vladisavljevic, Mun, & McClements, 2007), and polymers such as xanthan (Evison, Dickinson, Owusu-Apenten, & Williams, 1995). Incorporation of NaCl and polymer or glucose in the primary emulsion (Pawlik et al., 2010; Sapei et al., 2012), and levels of PGPR in the oil phase or addition thickener in the external aqueous phase have been shown to improve stability (Benichou et al., 2004; Dickinson, 2011). These approaches can sometimes improve not only the stability of the WOW emulsions, but also their resilience to change, particularly during processing, when the pH, osmotic, and chemical potential of the exterior aqueous phase can be subject to change.

In this manuscript we aim to demonstrate which are the key parameters controlling the stability and functionality of multiple emulsions. These include the low and high HLB emulsifiers, the effect of temperature and salt, and specifically the effect of gelling the internal water droplets using polymers requiring calcium or heat induced gelation, and investigating their stability under a range of conditions commonly found during food processing. This approach will hopefully improve their application in real systems, particularly for reduced fat food applications.

2. Material and methods

2.1. Materials

All materials were food grade and were used as received. Sodium Alginate (Flavicans HV) and a citric acid ester of monoglyceride (CITREM LR10, diglyceride enriched) were obtained from Danisco A/S (Copenhagen, Denmark). Sunflower oil and Vege-gel (carrageenan and locust bean gum) (Dr. Oetker) were purchased from a local supermarket (Norwich, UK). Lecithin (Optima Healthcare lecithin from soya beans) was purchased from a local food supplier (Holland and Barrett). The emulsifier polyglycerol polyricinoleate (PGPR 4125) was obtained from Palsgaard (Juelsminde Denmark). Sodium stearoyl lactylate (SSL) (M SSL3000) and distilled monoglycerides (Mono9512) was obtained from Puratos (Groot-Bijgaarden, Belgium). Liquid lecithin (prod no. Topcithin NGM) was obtained from Cargill (Vilvoorde, Belgium). A commercial Whey protein isolate (WPI) was used (Bipro, Davisco Foods International, Inc., Eden Prairie, MN). All the other ingredients (Span 20, Span 80, Span 85, calcium chloride, sodium chloride, xanthan gum, hydroxyethyl cellulose, glucose and sucrose) were purchased from Sigma–Aldrich (Poole, UK).

The emulsions were prepared in a Waring Commercial Laboratory Blender 8010 ES (Waring Laboratory Science, Winsted, CT, USA), using a mini container of 250 ml to prepare the single water in oil emulsions (WO) and a 1 L container in the preparation of multiple emulsions (WOW).

2.2. Preparation of single and multiple emulsions

Multiple emulsions containing water (W) or gel (G) in the internal phase (WOW or GOW) were prepared in a 2-step process. In the first step, single water in oil emulsions (WO) were prepared following a typical procedure in a blender cup where the oil phase was made of 48 g of sunflower oil and 1.6 g PGPR. It was then added to 35.75 ml of ultrapure water and the 2 phases were mixed in the blender for 30 s at low setting (up to 18000 rpm), let to rest for 30 s and then mixed again at high setting (up to 22,000 rpm) for another 30 s. In the preparation of emulsions with the internal phase gelled with alginate (GO), the same protocol as in the preparation of WO emulsions was followed but in this case instead of distilled water, a 1 wt% aqueous solution of alginate (29.5 g) was added to the oil phase. The gel was crosslinked after the first mixing cycle by adding 6.25 ml of 0.2 M calcium chloride prior to mixing all the components for 30 s at 22,000 rpm.

To prepare WOW or GOW emulsions, 21.25 g of the resulting single WO or GO emulsion from step 1 was added to 105 g of a 2 wt % lecithin solution prepared beforehand by dissolving 4 g of lecithin in 196 g of water and shaking the solution at 170 rpm in an incubator for 2 h at 30 °C. Then the emulsion was mixed in a blender at low setting for 30 s, let to rest for 30 s and mixed again at low setting for 30 s. The resultant double emulsion was then characterised in terms of size and morphology.

2.3. Yield measurements

Yield is the efficiency of the WOW emulsion to encapsulate the water droplets, expressed as percentage of emulsified water droplets remaining inside the secondary oil droplets (Dickinson et al., 1991). An inpermeant tracer dye, in this case (1,3,6,8-Pyrenetetrasulfonic acid – PTSA, Fisher Scientific, Loughborough, UK) was added to the original water phase used to make the WO emulsions. This WO emulsion is used is in turn to make the WOW emulsions. The WOW emulsion is centrifuged in a benchtop centrifuge at 10,000 × *g* for 10 min at 25 °C to remove the WOW droplets, and repeated on the subnatant to remove small droplets. The concentration of dye appearing in the continuous phase is measured spectrophotometrically at 375 nm against a calibration curve and hence the percentage of dye remaining encapsulated within the WOW emulsion droplets can be calculated. Yield values were taken as a function of storage time and emulsifier type. Measurements were made in triplicate, and the standard deviation was always better than ±2% Yield.

2.4. Characterisation of size and morphology

The size of the particles was measured by dynamic light scattering using a Zetasiser – nano zs (Malvern Instruments, Malvern, UK) and a Beckman-Coulter LS13320 Laser Diffraction Particle Sizer Analyser (Beckman Coulter(UK), High Wycombe, UK). The structure and morphology of the emulsions were studied by optical light microscopy (Olympus BX60 microscope, Olympus (UK), Southend,