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Effect of interfacial properties on the reactivity of a lipophilic ingredient in multilayered emulsions

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ABSTRACT

The aim of this work was to investigate the location and reactivity of a lipophilic spin probe, 4-phenyl-2,2,5,5-tetramethyl-3-imidazoline-1-oxyl nitroxide (PTMIO) in multilayered, biopolymer-based emulsions stabilized with a primary anionic layer (sodium caseinate) and a secondary cationic layer (lysozyme or diethylaminoethyl (DEAE) dextran). A broad range of ζ-potential values, from *ca.* −55 mV to 35 mV, was achieved. Emulsions with good physical stability were achieved when the magnitude of the net charge on the droplets was sufficiently great, otherwise some physical destabilization (flocculation) could be observed, especially in the case of caseinate-lysozyme-stabilized emulsions. The analysis of electron paramagnetic resonance (EPR) spectra of PTMIO in emulsion systems showed that probe molecules partitioned between the oil droplet core (*ca.* 73%) and the aqueous phase (*ca.* 27%), independently of the interfacial composition. Surprisingly, the rate of reduction of the nitroxide group of PTMIO by ascorbate anions remained unchanged when secondary interfacial layers were added, showing that the droplet surface charge was not the prevalent factor controlling the interactions between lipophilic compounds and aqueous phase reagents. Instead we argue that the reduction of PTMIO occurs in the aqueous phase.

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1. Introduction

A number of lipophilic ingredients (*e.g.*, flavors, pigments, vitamins, drugs) are added to food, pharmaceutical and cosmetic formulations to give desired functionality. Many of these require encapsulation strategies to allow them to be incorporated in aqueous-based systems and to remain stable. Microemulsions and emulsions are widely used as encapsulation systems because of their ability to allow dilution of these molecules in an aqueous continuous phase and to provide some chemical stabilization (Fathi, Mozafari, & Mohebbi, 2012; McClements, 2011; McClements, Decker, & Weiss, 2007; McClements & Li, 2010).

Droplet surface charge has also been repeatedly shown to affect metal-catalyzed oxidation of emulsified lipids containing unsaturated fatty acids (Mancuso, McClements, & Decker, 1999; Mei, Decker, & McClements, 1998), the degradation of flavor compounds (Choi, Decker, Henson, Popplewell, & McClements, 2010a) and the reactivity of lipophilic spin probes with ionic reagents (Berton-Carabin, Elias, & Coupland, 2013). The surface charge is thought to affect the interaction of reactive components in the aqueous phase (*e.g.*, metal ions) with the components in the lipid phase.

Perhaps surprisingly, while the effect of surface charge on the reactivity of lipophilic molecules has been clearly demonstrated when surfactants are used as emulsifiers, in protein-stabilized emulsions, the relationship is less clear (Berton, Ropers, Viau, & Genot, 2011; Hu, McClements, & Decker, 2003). For instance, Hu et al. (2003) showed that the oxidative stability of emulsified lipids was not correlated to the ζ-potential of emulsions stabilized by casein, whey protein isolate or soy protein isolate but instead argued the effects were due to differences in metal chelating and free radical scavenging efficiencies of the proteins. Alternatively, the physical homogeneity and thickness of the interface could also be an important factor governing the accessibility of the oil phase compounds to the aqueous phase reagents. This is in accordance with the recent findings of Berton-Carabin, Genot, Gaillard, Guibert, and Ropers (2013), who found that the higher the structural heterogeneity of reconstituted protein-based interfacial films, the higher the oxidizability of lipids in the corresponding emulsions.

In the past decade, substantial work has focused on tailoring emulsions with multilayered interfaces (Bouyer et al., 2011; Bouyer, Mekhloufi, Rosilio, Grossiord, & Agnely, 2012; Chen, Li, Ding, & Rao, 2011; Dickinson, 2009; Djordjevic, Cercaci, Alamed, McClements, &

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Decker, 2007; Gudipati, Sandra, McClements, & Decker, 2010; Guzey & McClements, 2007; Katsuda, McClements, Miglioranza, & Decker, 2008; Klinkesorn, Sophanodora, Chinachoti, Decker, & McClements, 2005; Lesmes, Sandra, Decker, & McClements, 2010; Lomova, Sukhorukov, & Antipina, 2010; Ogawa, Decker, & McClements, 2003; Taherian, Britten, Sabik, & Fustier, 2011; Zeeb, Gibis, Fischer, & Weiss, 2012). This is generally achieved by a layer-by-layer electrostatic deposition approach, which allows control of the physical properties of the interface (*e.g.*, charge, thickness). The number and composition of the interfacial layers can drastically change the physical and chemical stability of such emulsions. One of the main advantages of multilayered emulsions is their ability to improve the chemical stability of lipophilic components, especially the oxidative stability of unsaturated lipids (Djordjevic et al., 2007; Gudipati et al., 2010; Klinkesorn et al., 2005; Lesmes et al., 2010; Ogawa et al., 2003). Enhanced stability is generally associated with a cationic external interfacial layer, which would electrostatically repel transition metals ions from the droplet surface (Genot, Meynier, & Riaublanc, 2003; McClements & Decker, 2000). However, some findings contradict this model (Chen et al., 2011; Lomova et al., 2010), hence the exact mechanisms through which multilayered interfaces affect the reactivity of lipophilic components in O/W emulsions have yet to be fully elucidated.

Beyond interfacial characteristics, the properties of the aqueous phase of O/W emulsions (*e.g.*, the presence of non-adsorbed emulsifiers or colloidal structures) can greatly influence the reactivity of lipophilic molecules. This effect is due to the ability of such molecules or structures (*e.g.*, non-adsorbed proteins, surfactant micelles) to bind reactive molecules and hence modify their partitioning within the emulsion (Berton-Carabin, Elias, et al., 2013; Elias, McClements, & Decker, 2007; Nuchi, Hernandez, McClements, & Decker, 2002; Richards, Chaiyasit, McClements, & Decker, 2002). In particular, surfactant micelles can solubilize a fraction of lipophilic molecules that would otherwise locate within oil droplets and thus promote their accessibility to aqueous phase reagents (Berton-Carabin, Coupland, Qian, McClements, & Elias, 2012). In that case, the micelle properties (*e.g.*, charge) control to a large extent the reactivity of the lipophilic molecules.

In this work, we use a spectroscopic method to simultaneously determine the distribution and reactivity of a lipophilic solute in a multilayered emulsion. Primary emulsions were prepared using sodium caseinate, which has a negative charge at neutral pH, as an emulsifier. Multilayered emulsions were then formed by electrostatically depositing cationic biopolymers (lysozyme or a modified dextran) onto the caseinate-stabilized droplets. The spin probe 4-phenyl-2,2,5,5-tetramethyl-3-imidazoline-1-oxyl nitroxide (PTMIO) was used as a model lipophilic ingredient and its location and chemical reactivity within the emulsion system were determined by electron paramagnetic resonance (EPR) spectroscopy. In this study we develop novel multilayered emulsions stabilized exclusively with biopolymers and use them to study how the surface charge affects reactivity of a lipophilic ingredient in a polymer-stabilized emulsion.

2. Materials and methods

2.1. Materials

4-Phenyl-2,2,5,5-tetramethyl-3-imidazoline-1-oxyl nitroxide (PTMIO) was purchased from Enzo Life Sciences (Plymouth Meeting, PA, USA). Sodium L-ascorbate, diethylaminoethyl-dextran hydrochloride (DEAE dextran) and caseinate sodium salt from bovine milk were obtained from the Sigma Chemical Company (St. Louis, MO, USA). Sodium dodecyl sulfate (SDS) and sodium phosphate dibasic anhydrous were obtained from Fisher Scientific (Pittsburgh, PA, USA). n-Tetradecane (C14) was obtained from Alfa Aesar (Heysham, England). Ferric chloride hexahydrate was obtained from Mallinckrodt Chemicals (Phillipsburg, NJ, USA). Sodium phosphate monobasic was obtained from Acros Organics (New Jersey, NJ, USA). Lysozyme had been purified from hen egg white and was kindly donated by INRA (UR1268, Biopolymères Interactions Assemblages, France). The molecular structures of PTMIO and DEAE dextran are shown in Fig. 1.

2.2. Methods

2.2.1. Preparation of aqueous solutions of biopolymers

Aqueous solutions of sodium caseinate (30 g L^{-1}) and lysozyme (90 g L^{-1}) were prepared separately in phosphate buffer (100 mM, pH 7.0) and stirred overnight at room temperature. The rate of stirring was kept low to avoid foaming. The phosphate buffer used to prepare the solutions contained 200 μM PTMIO. Appropriate volumes of both solutions and of the same phosphate buffer were then mixed to achieve a constant concentration of sodium caseinate (10 g L^{-1}) and varied concentrations of lysozyme (0–30 g L^{-1}). The lysozyme to sodium caseinate mass ratio is henceforth referred to as *R*. The solutions were kept at room temperature under moderate magnetic stirring until analysis.

2.2.2. Preparation and physical characterization of emulsions

2.2.2.1. Preparation of emulsions. Sodium caseinate (30 g L^{-1}), lysozyme and DEAE dextran solutions (90 g L^{-1}) were prepared as described above. PTMIO (2 mmol kg^{-1}) was dissolved in n-tetradecane at 50 °C for 1 h then mixed with caseinate solution for 30 s using a high-speed blender (Brinkmann Polytron, Brinkmann Instruments Inc., Westbury, NY, USA) at 12,500 rpm to obtain a lipid concentration of 25 wt%. The emulsion premix was then passed through a microfluidizer (M-110Y Microfluidizer, Microfluidics, Newton, MA, USA configured with 75- and 200-μm interactions chambers in series) pre-heated at 60 °C (80 psi, 5 passes). After cooling down to room temperature, emulsion samples were mixed with lysozyme or DEAE dextran solutions along with phosphate buffer to produce emulsions with a final lipid concentration of 10 wt%, a final PTMIO concentration of 200 μmol kg^{-1} and a known added biopolymer to sodium caseinate mass ratio (referred as *R* in the following). Samples were stirred overnight at room temperature prior to analysis.

2.2.2.2. Particle size distribution. The emulsion droplet size distribution was measured immediately after homogenization and after 24 h storage at room temperature with a laser light scattering instrument (Horiba LA-920, Horiba Instruments Inc., West Chicago, IL, USA). Samples were diluted in distilled water to avoid multiple scattering effects. The relative refractive index of the dispersed phase was 1.08 with an absorption coefficient of 0.001. Some samples were mixed with SDS (4-fold dilution in 10 wt% SDS solution) prior to analysis to disrupt any flocs present. Results are reported as a full distribution or as surface mean diameter (d_{32}), defined as follows (Eq. (1)):

$$d_{32} = \frac{\sum N_i d_i^3}{\sum N_i d_i^2} \quad (1)$$

where N_i is the number of droplets corresponding to a given size category and d_i is the associated particle size.

To assess the polydispersity of emulsions, the span was calculated as follows (Eq. (2)):

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