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Effect of molecular exchange on water droplet size analysis as determined by diffusion NMR: The W/O/W double emulsion case

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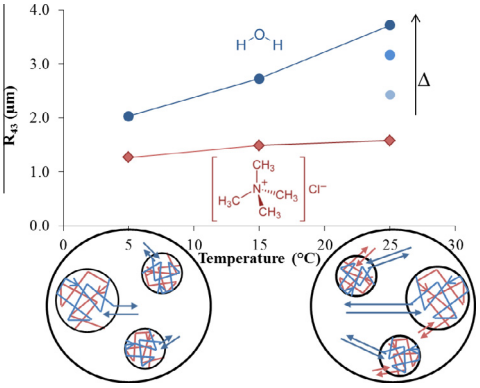
HIGHLIGHTS

- A multi-nuclear diffusion analysis of W/O/W emulsions was performed using diffusion NMR.
- The water diffusion signal was recorded by low and high-resolution NMR.
- The water-soluble marker diffusion signal was recorded by high-resolution NMR.
- Signal comparison enables the evaluation of molecular exchange.
- The accuracy of the estimated water droplet size of W/O/W emulsions was evaluated upon signal analysis.

GRAPHICAL ABSTRACT



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ABSTRACT

Hypothesis: The accuracy of the inner water droplet size determination of W/O/W emulsions upon water diffusion measurement by diffusion NMR was evaluated. The resulting droplet size data were compared to the results acquired from the diffusion measurement of a highly water soluble marker compound with low permeability in the oil layer of a W/O/W emulsion, which provide a closer representation of the actual droplet size. Differences in droplet size data obtained from water and the marker were ascribed to extra-droplet water diffusion.
Experiments: The diffusion data of the tetramethylammonium cation marker were measured using high-resolution pulsed field gradient NMR, whereas the water diffusion was measured using both low-resolution and high-resolution NMR. Different data analysis procedures were evaluated to correct for the effect of extra-droplet water diffusion on the accuracy of water droplet size analysis.
Findings: Using the water diffusion data, the use of a low measurement temperature and diffusion delay Δ could reduce the droplet size overestimation resulting from extra-droplet water diffusion, but this

Abbreviations: NMR, Nuclear Magnetic Resonance; pfg, pulsed field gradient; W/O/W, water-in-oil-in-water; TMACl, tetramethylammonium chloride.

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pfg-NMR diffusometry (pulsed field gradient)
Low-resolution NMR
High-resolution NMR

undesirable effect was inevitable. Detailed analysis of the diffusion data revealed that the extra-droplet diffusion effect was due to an exchange between the inner water phase and the oil phase, rather than by exchange between the internal and external aqueous phase. A promising data analysis procedure for retrieving reliable size data consisted of the application of Einstein's diffusion law to the experimentally determined diffusion distances. This simple procedure allowed determining the inner water droplet size of W/O/W emulsions upon measurement of water diffusion by low-resolution NMR at or even above room temperature.

1. Introduction

Water-in-oil-in-water (W/O/W) emulsions have the potential to create light foods as part of the oily dispersed phase is replaced by water [1]. In order to optimize the double emulsion formulation and to control its stability and functionality, the inner water droplet size distribution and internal water fraction can be determined. A wide range of emulsions in food process control and development have been characterized by low-resolution benchtop NMR [2]. The droplet size distribution of O/W, W/O, W/O/W and O/W/O emulsions can be determined using ^{1}H pulsed field gradient (pfg) NMR diffusometry [3–8]. Hereby, the droplet size distribution is estimated upon measurement of the restricted (intra-droplet) diffusion coefficient of molecules of the dispersed phase, followed by data analysis such as the procedure described by Murday and Cotts [9]. The latter procedure assumes that the droplet boundaries are impermeable. In addition, low-resolution NMR has also been applied to obtain information about the inner water volume fraction of W/O/W emulsions [6,10,11].

We have recently shown that molecular transport of water molecules through the oil layer of water-in-oil (W/O) emulsions can be detected using diffusion NMR [8]. This type of extra-droplet water diffusion was shown to become more important when raising the measurement temperature and NMR diffusion delay time Δ [6,8,12–14]. Extra-droplet water diffusion brought about an apparent increase in mean droplet size of W/O emulsions when using the Murday and Cotts data procedure [9], as well as when using the available data procedure that takes exchange into account [15]. These artefacts were unavoidable even when performing the diffusion analysis at low Δ and temperature. A data splicing procedure and the use of Einstein's diffusion law were proposed for determination of the droplet size, minimally affected by water exchange [8].

As W/O/W emulsions are more complex systems, it is interesting to evaluate whether the above mentioned instructs (i.e. low Δ and temperature) for minimizing the effect of extra-droplet water diffusion on the accuracy of water droplet size analysis also apply for W/O/W emulsions. For the same purpose, different data analysis procedures were evaluated. As a solid crystalline fat might suppress diffusion processes of water through the fat phase layer [16], the double emulsions were prepared either using a liquid oil or a solid fat.

To that end, both high-resolution NMR and low-resolution NMR, a more practical approach for measuring water diffusion, were applied. The former method enables the measurement of the spectrally-resolved diffusion signal of aqueous dissolved molecular species and water molecules in the water phases of W/O/W emulsions. Synchronous analysis of both signals allows the verification of the occurrence of molecular exchange. The water soluble tetramethylammonium chloride was selected, on account of an intense signal in a specific NMR region without overlap with water or oil, in addition to its low permeability through the oil phase due to its ionic nature [8,17–19].

To the best of our knowledge, this is the first simultaneous multi-nuclear temperature dependent diffusion analysis of water and a dissolved marker enclosed in W/O/W emulsion droplets as measured at different diffusion delays Δ using low-resolution and high-resolution pfg-NMR.

2. Materials and methods

2.1. Materials

The lipophilic emulsifier polyglycerol polyricinoleate (PGPR 4150; min. 75% n-glycerols with n = 2, 3 and 4; max. 10% m-glycerols with m $\geqslant$ 7) was kindly provided by Palsgaard A/S (Denmark). The hydrophilic emulsifier sodium caseinate (5.5% moisture; 96% protein on dry matter) was received as a gift sample from Armor Protéines (Saint Brice en Cogles, France), whereas Polysorbate 80 (Tween 80) was obtained from Sigma-Aldrich (Steinheim, Germany). High oleic sunflower oil (Hoso, Iodine Value = 87; 82% C18:1; SFC = 0% at 5 °C) was acquired from Contined B.V. (Bennekom, The Netherlands). Soft palm mid fraction (soft PMF; Iodine Value = 42–50; SFC = 79% at 5 °C) was purchased from Unigra Sp. (Conselice, Italy).

Tetramethylammonium chloride (TMACl, 109.6 g/mol) was obtained from Sigma-Aldrich (Steinheim, Germany). Deuterated water with a purity of 99.8 atom %D was purchased from Armar Chemicals (Switzerland). Food grade xanthan gum (FF) was a generous gift sample from Jungbunzlauer (Vienna, Austria). The 0.1 M phosphate buffer solution (pH 6.7) contained 0.02% (w/v) of the anti-microbial agent NaN_3 (Acros Organics, Geel, Belgium), KH_2PO_4 (Merck KGaA, Darmstadt, Germany) and K_2HPO_4 (Alfa Aesar, Karlsruhe, Germany). Unless stated differently, the above mentioned chemicals were of analytical grade.

2.2. Sample preparation

The inner (W_1) and outer (W_2) water phase of the $W_1/O/W_2$ emulsions that were investigated by both high and low-resolution NMR contained 800 mM TMACl in a mixture of D_2O/H_2O (50:50, wt%). In addition, the W_2 phase contained 0.2 wt% xanthan gum and 1.4 wt% Tween 80. The oil phase consisted of 2.5 wt% PGPR in Hoso. The W_1/O emulsions (40 g of 50:50, w/w) were mixed at 60 °C with an Ultra-Turrax (type S25KV - 25G, IKA®-Werke, Germany) at 6500 rpm for 4 min. The $W_1/O/W_2$ (30 g of 20:20:60, w/w) was prepared at room temperature upon mixing the W_1/O emulsion with W_2 phase with an Ultra-Turrax (type S25-10G, IKA®-Werke, Germany) at 9500 rpm for 1 min.

Regarding the composition of emulsions investigated only by low-resolution NMR, reference is made to the procedure described by Su et al. [20], which differs in the applied phase ratio and surfactant concentration. An Ultra-Turrax (type S 50 N - G 45 F, IKA®-Werke, Germany) and a Microfluidizer (type M110S, Microfluidics) at 840 bar (driving air pressure of 6 bar) for