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Trends in Food Science & Technology 20 (2009) 533–543

TRENDS IN FOOD SCIENCE & TECHNOLOGY

Review

Characterization of food emulsions by PFG NMR

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Due to its non-invasive nature and its ability to be implemented on downsized benchtop equipment, PFG NMR is gaining popularity as a droplet sizing tool in food emulsions. Food scientists and technologists should be aware of assumptions that are made with respect to PFG NMR methodology and mathematical models used for calculating droplet size distributions. This also needs to be considered when comparing results of NMR with other techniques. Several novel measurement and data modeling approaches have emerged that bring improvements in speed, sensitivity, accuracy and ability to probe dynamic events in real-time and *in-situ*.

Food emulsions

Water and lipids are critical for sustaining life and health, but their poor miscibility has posed a challenge for both nature and man. In most natural and processed foods, the immiscibility of water and lipids is overcome by dispersing one phase as droplets in the other phase (McClements & Weiss, 2005). In so-called water-in-oil (W/O) food emulsions, such as butters and margarines, water droplets are dispersed in a continuous phase of fat and oil. Examples of oil-in-water (O/W) food emulsions are dairy products such as milk and cheese, but also mayonnaises and dressings. Also multiple W/O/W and O/W/O food emulsions have been prepared, where within respectively oil and water droplets even smaller water and oil droplets are dispersed (Muschiolik, 2007). The manufacturing of some food emulsions such as butter has a long artisanal history, but nowadays sophisticated emulsification technologies are used, involving complex transformations such as phase inversions. Food emulsions are physically unstable by nature, and special precautions need to be taken to overcome the natural tendency to demix or break. A major part of the physical stability of food emulsions is determined by the continuous phase, but also the distribution of droplet sizes plays a role (McClements et al., 2005). For W/O food emulsions, the water droplet size distribution (DSD) also determines microbial stability (Verrips & Zaalberg, 1980). DSD's have also been associated with the rheological properties of food emulsions (Pal, 1996; Reiffers-Magnani, Cuq, & Watzke, 1999).

Due to its non-invasive nature, and ability to probe structures over a broad range of length scales, NMR has established itself as a tool for structural characterisation of food emulsions (Balinov, Mariette, & Soderman, 2003; Mariette, 2009). Within the arsenal of NMR techniques, Pulsed Field Gradient (PFG) based methods are most powerful for quantitative assessment of DSDs (Johns, 2009) and even long range order of droplets in structured emulsions (Balinov et al., 2003; Soderman, Lonnqvist, & Balinov, 1992; Soderman & Balinov, 1996). PFG NMR has found a range of practical applications in resolving relations between processing/storage and food emulsion functionality (Table 1). From Table 1 it becomes clear that NMR droplet sizing studies on food emulsions are predominantly carried out on low-field (20 MHz) spectrometers. The possibility to carry out droplet sizing on low-field and relatively low-cost NMR instruments has brought these measurements within the realm of product development and manufacturing (Guthausen, Todt, Burk, Schmalbein, & Kamlowski, 2008; Todt et al., 2001). In a food company such as Unilever, tens of benchtop NMR instruments are operational serving food technologists and scientists, food product developers and process operators with accurate DSDs with short turn around times.

Within this review we will outline the basic principles of PFG NMR, and how emulsion microstructure is reflected in PFG NMR decays. Issues with regard to extracting DSDs and other microstructural features will be discussed. Special attention will be given to concerns when tailoring PFG NMR to benchtop mode, as well as attempts to benchmark and validate PFG NMR against other measurement approaches.

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0924-2244/$ - see front matter
doi:10.1016/j.tifs.2009.07.001

Table 1. Overview of applied studies involving PFG NMR droplet sizing.

	Property	Field strength [MHz]	References
O/W	Temperature cycling stability	20	Bot, Duval, Duif, & Bouwman, 2007; Kiokias & Bot, 2005; Kiokias & Bot, 2006
	Oxidative stability	20	Kiokias, Dimakou, & Oreopoulou, 2007
	Rheology of O/W emulsions	300	Gabriele et al., 2009
	Oil bodies in seeds	400	Guillermo, 2007
	Oils droplet in cheese	60	Callaghan et al., 1983
W/O	Crystallisation inside droplets	20	Rousseau & Hodge, 2005; Hodge & Rousseau, 2005
	Storage stability	20	Rousseau, Zilnik, Khan, & Hodge, 2003 Hodge & Rousseau, 2003
	Water droplets in butters	20	Fourel, Guillement, & Lebotlan, 1995
	Water droplets in margarines	20	Balinov et al., 1994

PFG NMR measurements and diffusion, the basics

Principle of PFG NMR

The most basic pulsed field gradient NMR experiment consists of a spin-echo (SE) experiment with the 180° pulse in between the two equal gradient pulses of magnitude g and duration δ (Fig. 1). The first field gradient pulse introduces a dephasing in the proton precession frequency and the second pulse partially refocuses the phases. The phase difference leads to the attenuation of the NMR echo due to the diffusing spins that could not recover the initial phase. The signal loss in the case of unrestricted diffusion is proportional to the average root mean square displacements occurring between the two gradient pulses (Stejskal & Tanner, 1967). The SE sequence has the disadvantage that during the diffusion time the transversal (T_2) relaxation is active. This limits the duration of the diffusion time, thus in practice the Stimulated Echo (STE) sequence is used. In STE experiments relaxation is governed by T_1, which is typically longer than T_2, hence longer diffusion times can be used.

Restricted and hindered diffusion

It is well known that micro-structural information can be obtained by monitoring the diffusion of fluids in confined environments (Callaghan, 1993; Price, 1997). When the free motion of molecules during time Δ is limited by a boundary or obstacle, the molecular displacement is smaller as compared to free diffusion (Tanner & Stejskal, 1968). Fig. 2 represents different cases where diffusion within the dispersed or continuous phase can be exploited to infer information on emulsion microstructure. Intra-droplet restricted self-diffusion within a droplet (Fig. 2A) is most commonly exploited to infer DSD's. Typically, the phenomena of droplet self-diffusion and inter-droplet diffusion (Fig. 2B and 2C) are considered as complicating factors when modelling PFG NMR data for dispersed (droplet) liquids. We will show that these effects do however have their own merits for extracting microstructural features of food emulsions. Within double emulsions (W/O/W or O/W/O) several of the aforementioned diffusion mechanisms are active (Fig. 2D). Within the single dispersed phase, diffusion is restricted by the walls of the larger droplet, as well as the internal smaller droplets. Furthermore, often exchange can take place between internal droplets and continuous phase. Within the continuous phase, self-diffusion can be hindered by the droplet phase (Fig. 2E), and this can be exploited for obtaining information on long range order of droplets in emulsions.

Nomenclature of droplet size distribution

The number of occurrences of a particular value of a particle size can be expressed in various ways (Alderliesten, 1991), in terms of number of particles, cumulated diameters, surfaces or volumes of particles. In the literature on particle size analysis, very similar names or even identical are assigned to different mean diameters (Alderliesten, 2005). An unambiguous nomenclature (Alderliesten,

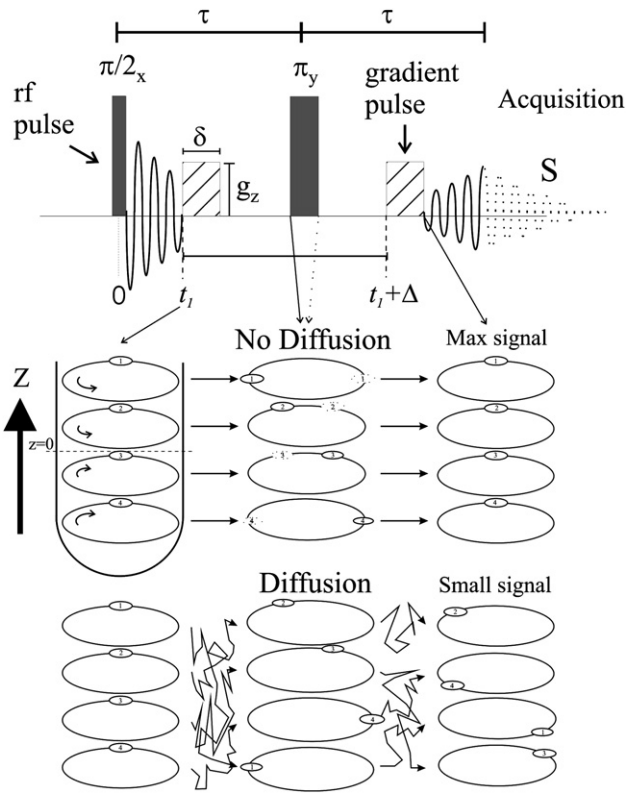

Fig. 1. Schematic representation of how a SE sequence measures self-diffusion (see text). Here δ is the gradient pulse duration, Δ is the diffusion time and g is the gradient strength. (Reproduced with permission from Price, 1997).