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Quantification of porous microstructures in partially frozen drops using magnetic resonance techniques

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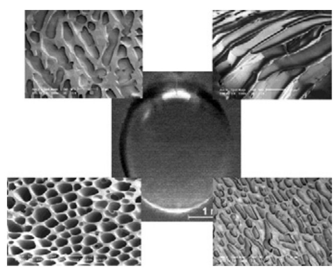
HIGHLIGHTS

- ► Non-invasive measurements of droplet ice microstructure for a range of solutes.
- ► Excellent comparison of NMR measurements with simulations in SEM lattice.
- ► Demonstration of real-time measurement of evolving ice microstructure.

GRAPHICAL ABSTRACT



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ABSTRACT

Nuclear magnetic resonance (NMR) measurements were shown to be able to non-invasively quantify the microstructure formed following freeze-concentration of (2 mm diameter) drops composed of a range of aqueous solutions (sucrose, fructose, coffee solution and NaCl). Specifically the surface-to-volume ratio and tortuosity of the resultant porous ice structures were uniquely quantified using pulsed field gradient (PFG) NMR measurements of restricted self-diffusion of the remaining unfrozen solution. These measurements were performed as a function of both solute concentration and freezing temperature. Validation was achieved via random walk self-diffusion simulations on SEM micrograph images of fracture planes through selected drops. Reasonably good agreement was produced between the NMR measurements and these simulations. A rapid version of the PFG measurement method was subsequently used to enable quantitative microstructure evolution measurements during the drop freezing process, as well as during subsequent ripening of the porous ice structure.

1. Introduction

Spray freezing refers to the solidification of liquid drops in a cold air stream [1]. It is a process that has been explored for the production of a range of systems including various foodstuffs [1], metal [2], biological cell preservation [3], pharmaceuticals [4] and proteins [5]. In the manufacture of foodstuffs, it has significant potential with respect to powder production with improved volatile retention. For the solidification of drops composed of aqueous solutions, partially frozen complex ice microstructures will generally form due to freeze concentration (which is the formation of ice from an aqueous solution, resulting in a more concentrated solute in the remaining solution); the ice can then be sublimed resulting in a highly porous structure. An ability to quantify the microstructure of such opaque drops non-invasively is highly desirable, in terms of both process and product quality control.

With respect to the freezing of suspended 1–3 mm diameter liquid drops (containing various solutes), we have previously demonstrated the use of nuclear magnetic resonance (NMR) techniques to quantify the kinetics of the freezing process [6] with

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