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Evidence of low-density water to high-density water structural transformation in milk during high-pressure processing

Bérengère Guignon [a,b,*], Eduardo Hidalgo Baltasar [a], Pedro D. Sanz [b], Valentín G. Baonza [a], Mercedes Taravillo [a]

[a] MALTA Consolider TEAM, Departamento de Química Física I, Facultad de Ciencias Químicas, UCM, Avda. Complutense s/n, 28040 Madrid, Spain
[b] MALTA Consolider TEAM, Departamento de Procesos, Instituto de Ciencia y Tecnología de Alimentos y Nutrición, CSIC, C/ José Antonio Nováis 10, 28040 Madrid, Spain

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A B S T R A C T

The objective of this research was to check whether the observed low-density water (LDW) to high-density water (HDW) transformation does take place or not in a complex aqueous system like those involved in high pressure processing of food. *In-situ* measurements of speed-of-sound up to 640 MPa were used for this purpose. After validation of the methodology in liquid water at 25 °C, LDW-to-HDW transformation was also evidenced in sodium caseinate solution and milk samples. The transformation pressure was always observed at 275 MPa. Since water plays a key role in most biochemical transformations, the occurrence of a LDW-HDW transition should be taken into account for understanding the complex component interactions in milk and other related systems under pressure.

Industrial relevance

Opportunities exist for the industry to use pressure as a tool for texturing dairy products. Process parameter choice to obtain a given texture is tricky due to the complexity of milk component interactions under pressure. As a main component in foods, water structural transformation under pressure should not be ignored by experts in the field.

1. Introduction

High-pressure processing of foods continues extending in the industry as a mild preservation treatment. Pressure effects are also interesting for texturing dairy products (Devi, Buckow, Hemar, & Kasapis, 2013). In spite of a great deal of researches in this field, food texture modulation by pressure treatment is still challenging. The mechanisms leading to a given texture observed after treatment are not fully understood.

In-situ techniques are useful to elucidate these mechanisms (Gebhardt, Takeda, Kulozik, & Doster, 2011; Tromp, Huppertz, & Kohlbrecher, 2014). Here, we introduce the use of ultrasonic measurements to address pressure-induced phenomena during high pressure processing of milk. In particular, we are going to focus on pressure-induced changes in water.

Liquid water has a short-range molecular structure. This structure emerges from the dynamic network formed by the hydrogen bonds between water molecules. It can be roughly considered that a given water molecule has four first neighbors arranged in a quasi-tetrahedral way around it (first shell), and other four neighbors at a higher distance (second shell). When pressure is increased, the second shell collapses into the first one and the hydrogen bonding network is strongly modified (Okhulkov, Demianets, & Gorbaty, 1994). As a result, a pressure-driven structural rearrangement of water takes place in the liquid phase. This is known in the specialized literature as the Low-Density Water (LDW) to High-Density Water (HDW) structural transformation (Soper & Ricci, 2000). It was shown by both calculations and experiments that water exhibits such transformation between 200 MPa and 300 MPa at room temperature (Fanetti et al., 2014; Li et al., 2005; Marco Saitta & Datchi, 2003).

Since these pressure-temperature conditions are commonly achieved during high pressure processing of food, the question that arises is whether such structural transformation also happens in more complex aqueous systems (*e.g.* milk). This is an important question because it has long been suspected that water gets involved in protein denaturation and changes in casein micelles under pressure (Huppertz & de Kruif, 2006), and both phenomena have an impact on dairy product texture; however, water implication in such phenomena has not been strictly demonstrated yet.

Here our goal is to seek for evidences of such structural transformation in milk under pressure. For this purpose, we first demonstrate how LDW-to-HDW transformation can be detected in pure water by ultrasound measurements, and later, we shall check whether it is observed or not in two selected complex systems of interest in food industry: sodium caseinate solution and pasteurized skimmed milk.

* Corresponding author at: MALTA Consolider TEAM, Departamento de Química Física I, Facultad de Ciencias Químicas, UCM, Avda. Complutense s/n, 28040 Madrid, Spain.
E-mail addresses: bguignon@ucm.es (B. Guignon), eduardohidalgobaltasar@gmail.com (E. Hidalgo Baltasar), pedro.sanz@csic.es (P.D. Sanz), vgbaonza@quim.ucm.es (V. G. Baonza), mtaravil@quim.ucm.es (M. Taravillo).

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2. Material and methods

2.1. Samples

Deionized water type I (electrolytic conductivity ~0.05 μS·cm^{-1}, Milli-Q system, Millipore, Billerica, USA) was employed in the experiments.

Sodium caseinate solution was chosen to start the study in complex systems because it is comparatively less complex than milk and because of its importance in the dairy sector for cheese making and as an additive in foods. The aqueous solution of sodium caseinate (Ref. C8654 - from bovine milk, batch no. 117K0138, Sigma-Aldrich, New Zealand) was prepared at a mass fraction of 0.026 which is the mean casein concentration in milk. Moisture content of sodium caseinate was taken into account (6.2% dry basis from thermogravimetric analysis). The caseinate powder was dissolved in deionized water by continuous stirring at room temperature the day before the experiments.

The study was then pursued with milk (Puleva, local supermarket, Spain). Milk was chosen skimmed and pasteurized to minimize the potential interferences of pressure-induced phenomena other than water transformation (*e.g.* fat crystallization, casein micelles disruption and whey protein denaturation) during the measurements (Harte, Gurram, Luedecke, Swanson, & Barbosa-Cánovas, 2007). The claimed composition was 4.7 g of carbohydrates, 3.1 g of proteins, 0.3 g of fat, and 110 mg of calcium for 100 mL of milk.

2.2. Ultrasonic measurements

The speed of sound in the samples was measured *in situ* as a function of pressure employing the same experimental setup as described in a previous work (Hidalgo Baltasar, Taravillo, Baonza, Sanz, & Guignon, 2011). This setup has the particularity to cover the intermediate pressure range between 100 and 700 MPa in comparison to commercial devices (usually limited to 300 MPa) and diamond anvil cell (usually used above 1000 MPa).

The experimental procedure for measurements consists of: sample holder filling (about 15 mL of sample), ultrasonic cell setting up, vessel load and closing, thermal equilibration, pressure increase step by step (either 10 MPa or 20 MPa steps), and final decompression. At each step, pressure, temperature, and ultrasound signal are simultaneously recorded. The maximal combined standard uncertainties are estimated to be 0.2 °C in temperature and 3.2 MPa in pressure. Speed of sound is calculated from the ratio between the wave travel path and the time of flight. Both parameters are obtained exactly in the same way as explained in detail earlier (Hidalgo Baltasar et al., 2011). Experiments were repeated three times. The combined standard uncertainty in speed of sound is estimated to be between 2 m·s^{-1} and 4 m·s^{-1}.

2.3. Data treatment

Numerical analyses of the results (signal analysis, non-linear curve fitting) were performed using OriginPro 8.0 package (OriginLab Corporation, Northampton, MA, USA).

3. Results and discussion

3.1. Determination of HDW-to-LDW transformation by ultrasound measurements

The study of pure liquid water is the first step and a key step in the understanding of most food systems submitted to different temperature and pressure conditions. This is still also one of the biggest challenges to scientists and technologists since it is well known that many of its static and dynamic properties present an anomalous behavior. Among the anomalies found in the structural properties of water at the molecular level, the LWD-to-HDW transformation is one of the most intriguing. Despite it has been studied by different techniques (Fanetti et al., 2014; Li et al., 2005; Marco Saitta & Datchi, 2003), the knowledge about this transformation remains incomplete. Here we study it by means of acoustic measurements since the speed of sound gives simultaneous information on several thermodynamic properties (specific heat, thermal expansion coefficient) and, in particular, on density (Guignon & Baonza, 2016).

Speed of sound was determined in water as a function of pressure at 25 °C. The results are shown in Fig. 1. Speed of sound in water increases with pressure in a non-linear way. Because the liquid becomes denser, the ultrasonic wave is transmitted faster under pressure. An excellent agreement is found with reference data: fractional deviations from IAPWS-95 formulation are below 0.5%.

Speed of sound is related to density ρ and adiabatic compressibility κ_s through the Newton-Laplace equation:

$$w = \sqrt{\frac{1}{\kappa_s \cdot \rho}} \tag{1}$$

And by definition:

$$\kappa_s = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial p}\right)_s \tag{2}$$

Therefore, we can easily compute density change with pressure from the speed-of-sound measurements:

$$\left(\frac{\partial \rho}{\partial p}\right)_s = \frac{1}{w^2} \tag{3}$$

This is plotted in Fig. 2a in density unit (s^2·m^{-2} = 10^6·kg·m^{-3}·MPa^{-1}). The rate at which density increases with pressure continuously decreases also in a non-linear way.

The pressure dependencies of both w and $1/w^2$ are smooth and there are no obvious changes with pressure. However, if we evaluate the pressure derivative of $1/w^2$, two asymptotic linear trends are observed (Fig. 2b). The derivative is numerically computed as follows:

$$\Delta\rho'(p_i) = \frac{1}{2}\left(\frac{\rho'_{i+1}-\rho'_i}{p_{i+1}-p_i} + \frac{\rho'_i-\rho'_{i-1}}{p_i-p_{i-1}}\right) \text{ with } \rho'_i = \left(\frac{\partial \rho}{\partial p}\right)_S \text{ at } p = p_i \tag{4}$$

Although this differential expression unavoidably leads to an increase of uncertainty, the low experimental uncertainty of the raw data and the small pressure derivation step used in calculations still allow obtaining a semi-quantitative picture of the studied phenomena. The uncertainty in $\Delta\rho'$ is estimated to be below 4 · 10^{-5} kg·m^{-3}·MPa^{-2} (law of propagation of uncertainty).

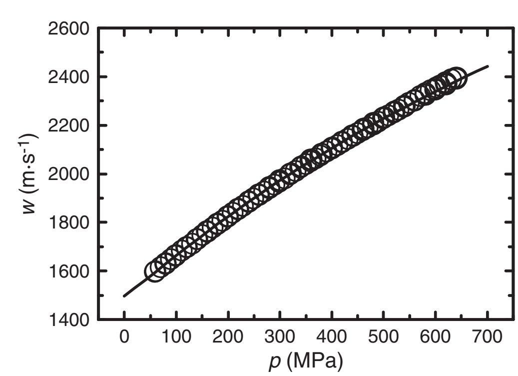

Fig. 1. Measured speed-of-sound in water as a function of pressure compared to IAPWS-95 formulation (solid line, water equation-of-state from Wagner & Pruss, 2002).