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Water-holding capacity and structure of hydrocolloid-gels, WPC-gels and yogurts characterised by means of NMR

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Abstract

The objective of this work is to illustrate the possibilities of NMR (nuclear magnetic resonance) for characterising gels. As model food systems, carrageenan-gels/solutions and whey protein gels are studied. The water-holding capacity of gels including sol-gel transitions is investigated. Pore systems of gels are characterised by analysed diffusion experiments. Yogurt is used as an example of a complex food, and is treated with a special wash-out-test. This test allows conclusions concerning the trend to syneresis and the structure of the system. It is shown that NMR provides a powerful tool for tackling practice-relevant problems, such as syneresis, sandy mouth-feel or increased yield and to improve or develop appropriate processes.

Keywords: Water-holding capacity; Hydrocolloid-gels; WPC-gels; Yogurt; NMR

1. Introduction

The bonding-type of water and the mobility of water molecules are relevant in food process technology with regard to yield, sensory evaluation, stability (in physical terms), texture and processing. Hydrocolloids are used for the production of many dairy products (e.g. jellied products, desserts and puddings, yogurt, cocoa and ice-cream) in order to modify the properties of the product in a predetermined manner. Thus, for example, the viscosity can be increased, gel-structures can be created or the physical stability can be lengthened.

The problem is that foods are multi-phase systems, such as suspensions, emulsions and foams. Interactions of ingredients are of great practical importance. Hydrocolloids, for example, might have negative effects due to possible interactions with milk-proteins. Miscibility, complex coacervation or incompatibility, which eventually lead, for example, to syneresis or sandy mouth-feel can occur.

Nuclear magnetic resonance (NMR) is already applied in food technology for process and quality control, research and development. In the present work the possibilities of NMR for characterising, both qualitatively and quantitatively, the structure and water-holding capacity of hydrocolloid-gels are demonstrated. Generally there are four possibilities for characterising gels by means of NMR:

- Determination of characteristic viscosities of hydrocolloid-systems by means of T_2 relaxation times
- Characterisation of the water-holding capacity of gels including sol-gel transitions, phase-separation and syneresis
- Detection of the denaturation of proteins
- Analysis of the pore system of gels with diffusion experiments.

In this work, gels were studied by means of T_2 relaxation times and diffusion experiments.

2. Material and methods

2.1. Material

As model food systems carrageenan gels/solutions and whey protein gels were studied. Carrageenan gels were made of a commercial hybrid-carrageenan (kappa- and iota-monomers) used in dairy-products, pure kappa-carrageenan (Aldrich Chemical Company, Inc., USA), pure iota-carrageenan (Aldrich Chemical Company, Inc.,

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USA) and pure lambda-carrageenan (Aldrich Chemical Company, Inc., USA). 3 w/w-% carrageenan gels were dispersed in distilled water and stirred for 20 min at 70 °C. The whey protein concentrate (WPC) gels were made of 15 w/w-% whey protein powder (Bayerische Milchindustrie eG, Landshut, Germany) dispersed in distilled water and heated for 10 min at 85 °C in order to denature the whey proteins. One WPC-solution was adjusted to pH 9.5 with NaOH; another one was adjusted to pH 5.4 with HCl. 200 mg resp. 2000 mg $CaCl_2$ were added to two WPC-solutions in order to reinforce the gelling.

Yogurt was used as an example of a complex food. Table 1 shows the studied recipes.

2.2. Methods

The gels and solutions were studied by means of NMR. In NMR the magnetisation $\vec{M}$ is proportional to the proton density N in the material and inversly proportional to the absolute temperature T. By means of the temporal development of the proton density (^1H) it is possible to specify the moisture per volume and, with the help of the relaxation times (T_1, T_2), the bonding-type of water (free or immobilised water). If it is possible to differentiate between several phases, the volume fraction and bonding-type of a phase can be determined.

Yogurt was treated with a special wash-out-test. For this test, yogurt was put in special glass-tubes (Fig. 1). T_2-experiments were performed with yogurt. The water, in open tubes was substituted with D_2O by opening the screw and putting D_2O onto the specimen. Afterwards, the T_2-experiment was performed again. This test allowed conclusions about the trend to syneresis and the structure of the system.

Self-diffusion coefficients and restricted diffusion can be determined using pulsed gradients. It is possible to derive, from these, a characteristic pore length.

For all T_2-experiments, a low-resolution NMR spectrometer system, MINISPEC mq20 (Bruker Analytik GmbH, Rheinstetten, Germany), was used. The resonance frequency of ^1H is 20 MHz. The diffusion experiments were performed in a magnet SWB 200 (Bruker Analytik GmbH, Rheinstetten, Germany). The static magnetic field B_0 is 4.7 Tesla which corresponds to a proton frequency of 200.13 MHz.

3. Results and discussion

3.1. Water-holding capacity

The water-holding capacity is determined by many different measuring methods, which are based on different measuring principles and conditions. Most of the methods are destructive and the microstructure is

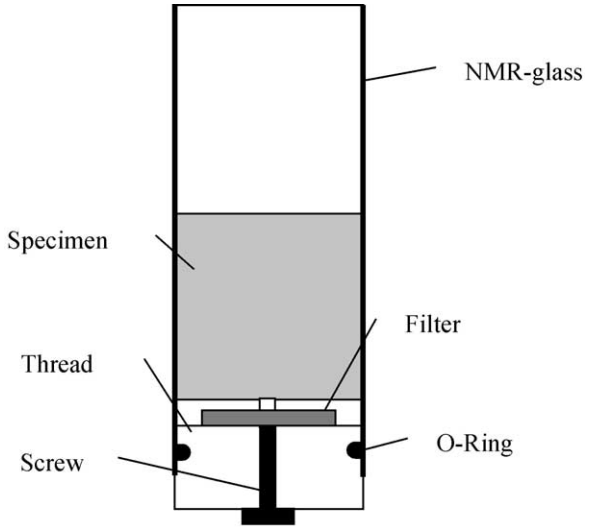

Fig. 1. Wash-out-test NMR-glass-tube.

Table 1
Recipes and processing of studied yogurts

Yogurt	Milk pretreatment	Heat treatment	Hydrocolloid	Fermentation
P	Pasteurised, homogenised	30 min, 90 °C	–	*Lactobacillus delbrückii* ssp. *bulgaricus, Streptococcus salivarius* ssp. *thermophilus*
PC	Pasteurised, homogenised	30 min, 90 °C	Kappa-carrageenan	*Lactobacillus delbrückii* ssp. *bulgaricus, Streptococcus salivarius* ssp. *thermophilus*
R	Raw milk	30 min, 65 °C	–	*Lactobacillus delbrückii* ssp. *bulgaricus, Streptococcus salivarius* ssp. *thermophilus*
RC	Raw milk	30 min, 65 °C	Kappa-carrageenan	*Lactobacillus delbrückii* ssp. *bulgaricus, Streptococcus salivarius* ssp. *thermophilus*
M (Merchandise)	Unidentified	Unidentified	Unidentified	Unidentified

mainly ignored. In contrast, NMR is non-destructive and considers the microstructure. Fig. 2 shows the relaxation times T_2 of 3 w/w-% carrageenan in distilled water. The larger the T_2, the larger the mobility. Carrageenan solutions therefore show, higher relaxation times than carrageenan-gels. The different relaxation times of the gels can be described by the different properties of the gels. The relaxation times, T_2, of the solutions are analogous to their voluminosity. The voluminosity means the amount of "bound"/immobilised water. In gels, in contrast to solutions it is not rheometrically determinable.

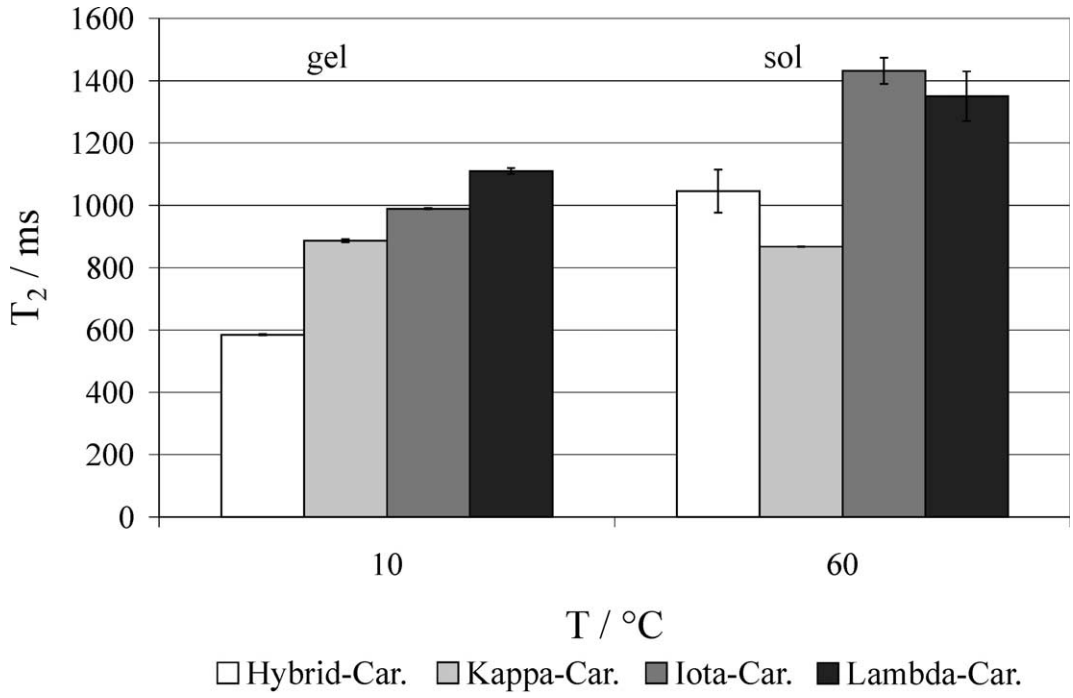

Fig. 2. Relaxation times T_2 of 3 w/w-% carrageenan in distilled water.

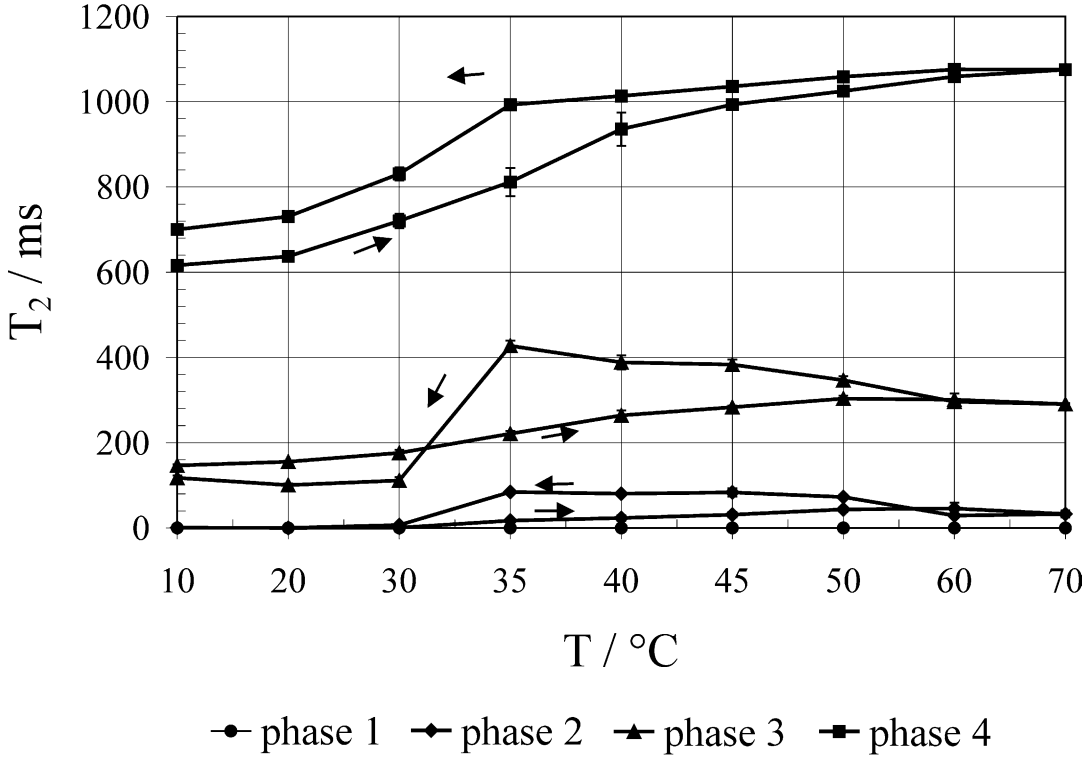

Fig. 3. Temperature-profile of 3 w/w-% hybrid-carrageenan in distilled water.

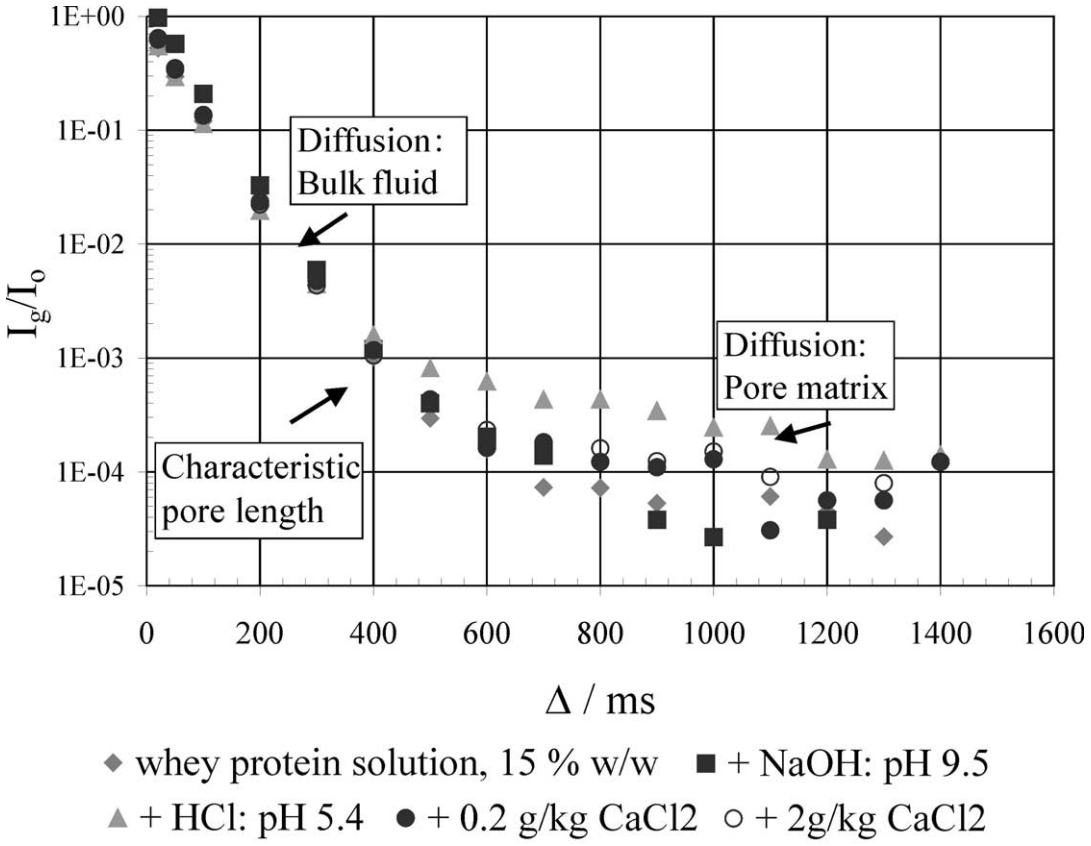

Fig. 4. Diffusion experiments of whey protein solutions.

To differentiate between gelling carrageenans and only viscosity-increasing carrageenans, it is possible to look at the temperature-profile of the hydrocolloids (Fig. 3). In this profile, four phases can be proven. The mobility of the phases increases from phase 1 to phase 4. If the carrageenan is able to form a gel, like kappa-carrageenan, iota-caarrageenan or the used hybrid-type, a hysteresis can be observed in phases 2–4. Phase 1, which is the solid and immobilised phase, does not seem to be involved in the gelling process. Lambda-carrageenan, which is only viscosity-increasing, shows no hysteresis in its temperature-profile.

NMR allows determination of the water-holding capacity, and the voluminosity and differentiation between gelling agents and viscosity-increasing hydrocolloids.

3.2. Diffusion experiments

The diffusion experiments of whey protein gels in Fig. 4 show that it is possible to differentiate between diffusion in bulk fluid and in pore matrix. From the inflexion point, the characteristic pore length is calculable. By means of the pore size it is possible to draw conclusions about the microbiological stability of the specimen. The permeability influences important product-properties in food technology, such as syneresis and filtration behaviour.

3.3. Influence of recipe and processing on water-holding in yogurt

The influence of the recipe and processing on water-holding, and determination by means of NMR, was shown for different yogurts. The results of the combination of wash-out-test and T_2 relaxation times are shown in Fig. 5. It can be seen that, depending on recipe and processing, the distribution of the ratio of the phases is different. The samples also show differences between the yogurts in the water content after washing out the capillary water. The high standard deviations indicate an inhomogeneous structure.

The results help to identify the structure of the gel matrix and the phases which should be modified by processing or additives in order to prevent syneresis.

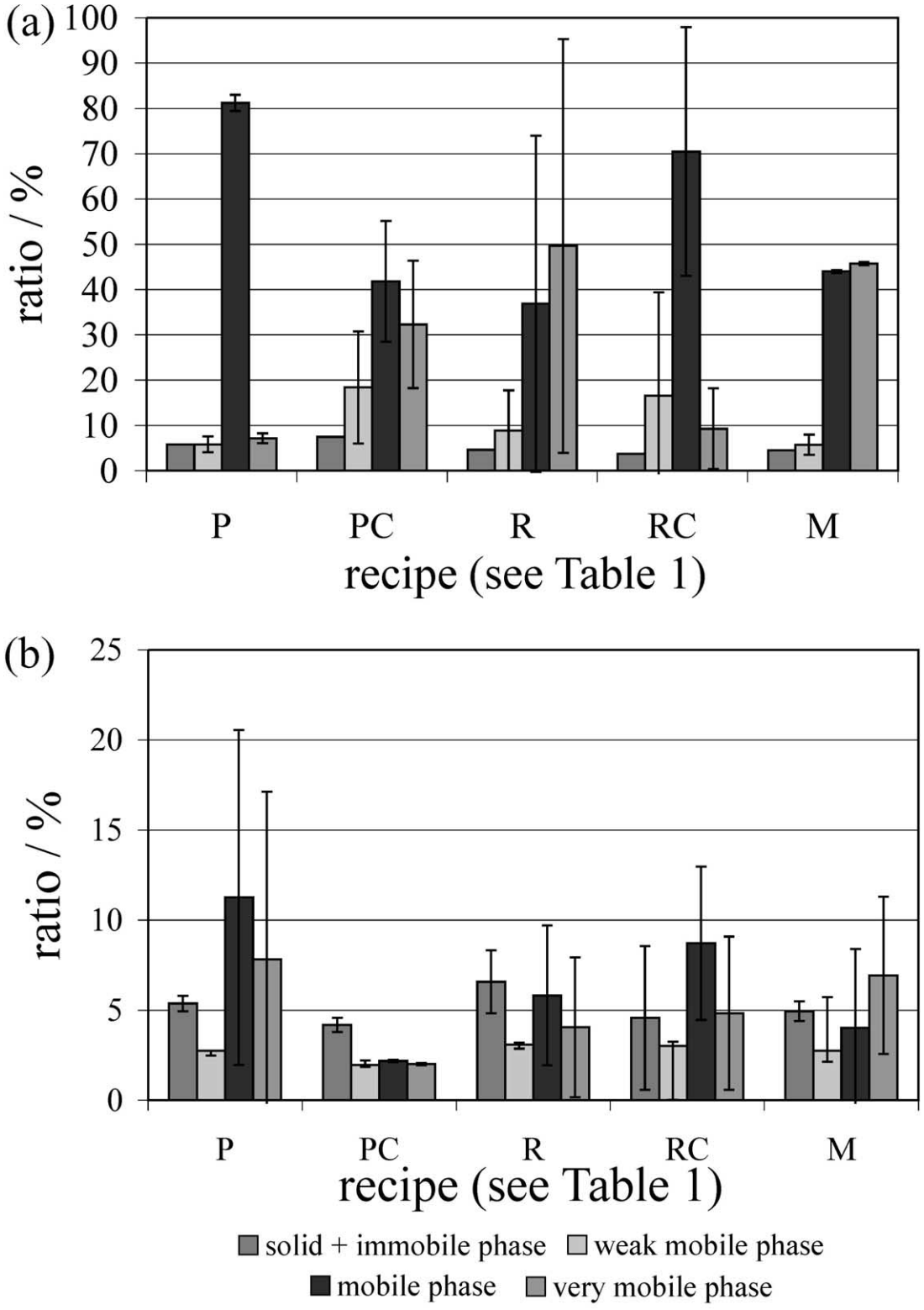

Fig. 5. Water-holding of yogurts as a function of the recipe and the processing to recipe and processing: ratio of phases (a) before and (b) after wash-out-test.

4. Conclusions

NMR offers microscopic information about the structure of gels, and helps to quantify the influences of ingredients and processing and to characterise the water-holding capacity of gels. The advantages of applications of NMR in food technology are:

- Short measuring times, little or no preparation
- On-line measurement possible: viscosity, water-holding capacity, denaturation
- More information about microstructure than other methods (e. g. rheology).

Overall, therefore, NMR provides a powerful tool for tackling practice-relevant problems, such as syneresis, sandy mouth-feel or increased yield and for improving or developing appropriate processes.

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Further reading

Harz, H.-P. (1987). Untersuchungen zum Gefrierverhalten flüssiger Lebensmittel im Hinblick auf das Gefrierlagern, Gefriertrocknen und Gefrierkonzentrieren. PhD thesis, Universität, Karlsruhe.

Liebenspacher, F. (1991). Untersuchungen über Wassersorption und den Wassertransport in Packstoffen auf Zellulosebasis. PhD thesis, Technische Universität, München.