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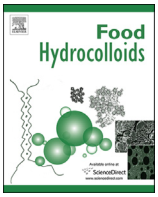

Water holding capacity and swelling of casein hydrogels

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ABSTRACT

The water holding capacity of casein gels was investigated by measuring the swelling and de-swelling under a variety of conditions of temperature and salt concentration. Transglutaminase cross-linked sodium caseinate (15% w/w) gels will swell in good solvents or shrink in poor solvents until an equilibrium casein volume fraction is reached, and this is determined by the cross-link density. The results are interpreted using extended Flory–Rehner theory for weak polyelectrolytes. NaCl and $CaCl_2$ solutions tend to shrink the gels through the decreased Donnan pressure. In contrast, high volume fraction renneted casein (48% w/w) gels tend to swell in NaCl and $CaCl_2$. These results are consistent with theory since the equilibrium volume fractions appear to be at an intermediate value (estimated about 20%). Experiments on casein micelles, which can be considered nano-gels, show the same behavior and trends. Physically cross-linked gels such as a highly concentrated renneted casein gel and casein micelles show the same (de-)swelling behavior. Cross-linked caseinate gels (15% w/w) have a lesser tendency to swell due to the lower casein volume fraction. Physically cross-linked gels will eventually completely dissolve in a good solvent. The results presented give a clear picture of the parameters that determine the equilibrium water content of a food polymer gel.

1. Introduction

The water holding capacity of a food gel is of relevance for its stability, microbial safety, functional properties, texture and last but not least the cost of production. Although a number of methods exist to measure water holding capacity (see for example the review by Kneifel, Paquin, Abert, and Richard (1991) who list a wide range of techniques), most studies have defined water holding capacity as the residual water in a centrifuge pellet. The centrifugal method was used for instance by Creamer (1985) and Kocher and Foegeding (1993).

However, it was felt that the centrifugal method measures gel strength rather than water holding capacity as the result depends on the applied *g*-force. It is for this reason that we developed a new method to characterize the water holding capacity of food hydrogels. For this we relied on methods to measure the swelling or shrinking behavior of polymer gels. The axiom is that if a gel does not want to “suck” up the water it will expel water (synerese). In other words if thermodynamics are unfavorable, water will be expelled. Of course many food products are thermodynamically unstable and only stable in kinetic terms.

Here we will investigate the thermodynamics of the water holding capacity of casein gels in relation to kinetics of swelling and de-swelling. We think that the methods presented herewith are applicable to other food polymer (hydro) gels such as gelatin, carrageenan, xanthan and fibrous protein gels.

2. Theoretical background

It was Flory and Rehner (1943) (FR) who developed a theory for the swelling of neutral polymer gels in a-polar solvent. The basic thermodynamic idea is that if polymer strand is immersed in a good solvent it will gain mixing and configurational entropy and as a result the gel takes up solvent. The swelling, however, stretches the polymer strands between the chemical cross-links and configurational entropy diminishes. When the mixing entropy balances the loss in configurational entropy the system is in equilibrium. If the mixing is non-ideal then enthalpic terms come into play as well, just as in FR theory. Tanaka (1978) and Shibayama and Tanaka

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(1993) were some of the first to systematically investigate (weak) polyelectrolyte gels and show experimentally that there can be a first order swelling to shrinking transition. There are now several review papers on this topic (Quesada-Perez, Alberto Maroto-Centeno, Forcada, & Hidalgo-Alvarez, 2011; Schneider & Linse, 2004; Shibayama & Tanaka, 1993).

2.1. Equilibrium swelling

The Gibbs free energy of a gel is composed of three contributions.

$$\Delta G = \Delta G_{\text{mix}} + \Delta G_{\text{ion}} + \Delta G_{\text{el}}$$

$$\Delta G = \Delta H - T\Delta S + \pi \text{d}V$$

$$\pi = \frac{-\text{d}\Delta G}{\text{d}V} \quad \text{at } T,\ n_i \text{ constant}$$

$$\pi_{\text{tot}} = \pi_{\text{mix}} + \pi_{\text{ion}} + \pi_{\text{el}}$$

where ΔG is minimal when the system is in equilibrium and therefore $\pi_{\text{tot}} = 0$. The symbols have the usual thermodynamic meaning. The subscript refers to the following contributions. The term π_{mix} comes from the mixing free energy of a (neutral) polymer chain with the solvent and is therefore the solvency of the neutral polymer (the osmotic pressure of the "bare" polymer network, like rubber in an organic solvent). The term π_{el} comes from the elastic deformation of the network restricting the configurations of the polymer strand. The term π_{ion} comes from the presence of ions. This aspect was not part of the original FR theory but added later, and accounts for the difference in number of ions inside the gel (as counter ions) and in the outside bath. Therefore π_{ion} is the DIFFERENCE in osmotic pressure inside and outside the gel and is called the Donnan pressure. The explicit expressions for each of the terms can be found in the given references; however, for the Donnan pressure we used the expressions given by Philipse and Vrij (2011). NOTE: this all assumes a system at equilibrium.

To illustrate the calculation we present a plot in Fig. 1 of the three contributions as a function of polymer volume fraction and at one salt concentration (0.2% w/w about 33 mM). Note: these are model calculations based on the theoretical equations presented above and are meant to illustrate the theoretical background. The equilibrium situation is $\pi(\varphi, 0.2) = 0$, so at $\varphi \approx 0.11$. If the sample in Fig. 1 is at polymer volume fraction of say 0.15 the gel will tend to swell, i.e. lowering polymer volume fraction. However at a volume fraction of 0.05 it will shrink. It must be mentioned here that the theory assumes chemical and permanent cross-links. For some of our systems the cross-links are of a physical nature. For example, calcium and hydrogen bridges or hydrophobic bonds. However the basic ideas and concepts remain the same.

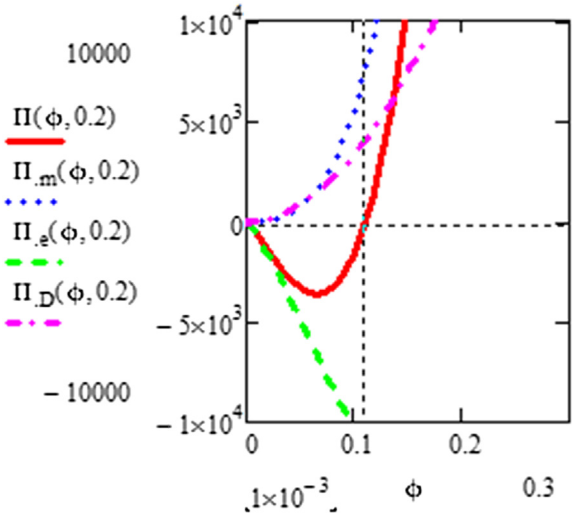

Fig. 1. Osmotic contributions (Pa) to a casein hydrogel in a 0.2 M NaCl solution as a function of casein volume fraction.

2.2. Kinetics of swelling

There are a few models that describe the swelling kinetics of polyelectrolyte gels (Ganji, Vasheghani-Farahani, & Vasheghani-Farahani, 2010; Quesada-Perez et al., 2011; Schneider & Linse, 2004; Shibayama & Tanaka, 1993). Here we will use the expression of Shibayama and Tanaka (1993). These authors describe the swelling of a polymer gel by calculating the increase in radius $\Delta a(t)$ as a function of time for a spherical gel:

$$\Delta a(t,\tau) := 6\cdot\frac{\Delta a_0}{\pi^2}\cdot\sum_{n=1}^{1}\left(n^{-2}\cdot\exp\left(-n\cdot\frac{t}{\tau}\right)\right) + a_{\text{d}}\cdot t$$

The final or equilibrium radius is a_{f}. The relaxation time, τ, determines the kinetics. We have used only one relaxation time and thus $n = 1$. The last term in this equation, $a_{\text{d}}\cdot t$, was added by us. This term accounts for the fact that we observed in non-cross-linked gels a slow but continuous dissolution of the surface of the gel. Actually one would expect that a physical gel dissolves in a good solvent. Since the dissolution process was slow and can occur at the surface only we assumed that dissolution changed (diminished) the radius linearly with time with a coefficient a_{d}.

Δa_{o} represents the total change in radius. Thus $\Delta a_{\text{o}} = a_{\text{f}} - a_{\text{ini}}$, where a_{ini} is the initial radius. Using this we can calculate the relative volume change, FY (t, τ), of the spherical gel as a function of time and relaxation time:

$$\text{FY}(t,\tau) := \left[\frac{a_{\text{f}} - \Delta a(t,\tau)}{\left(a_{\text{f}} - \Delta a_0\right)}\right]^3$$

In actual fact we did not use spherical gels but small cubes of about 1 cm^3. This would modify the equations as given by Shibayama and Tanaka (1993). However, for our purposes the spherical expression suffices because we aim to understand the underlying physics and the differences between spheres and cubes are rather small.

3. Materials and methods

3.1. Experimental materials

We used several different casein gels:

1. A 15% sodium caseinate (NaCN) solution was adjusted to pH 5.7 and cross-linked using transglutaminase (Ex Ajinomoto, Hamburg Germany, transglutaminase concentration of 50 units in the powder state) at a concentration of 1% w/w at room temperature. This resulted in a transparent gel from which we cut cubes of about 1 cm^3. This is a chemically cross-linked gel and called XL-NaCN.
2. A renneted caseinate (RC) gel with a high dry matter content of 48% and pH = 5.7. About 1 cm^3 cubes were cut from a large slab.